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89		8 8	1933, **10**, 500.	1930, **7**, 503.
171	Table II, Column 2,	3	0·5598 g.	0·0550 g.
,,		4	0·6673	0·0667 g.
249		3	Rosaniline, etc.	*p*-Rosaniline, etc.
252	Table III		Do	Do
322		5*	353°	350°
324		1	the gel contained	the hydrolysis of CCl_4 ceased. At this stage the gel contained
,,		4	2·6	2·7
324		13	119°	100°
,,		14	0·204	0·004
,,	Table II, column 9	2*	4·92	4·02
325	Do. column 2		330	300
325	eq. (*i*)	3	CO	CO_2
,,		10*	Column 2	Column 11
327		6	**35**	**36**
328	Table I, column 3	1	H_2	H_2O
,,	Do. column 3	2*	9·05	0·05
,,	Do. column 4	2*	11·08%	11·68%
,,		18*	$(C_1 - C_2) - 100$ long. *g*	$(C_1 - C_2)/100$ g.
329	Table II, column 6	1	0·29	0·99
,,	Do.	2*	1·06	1·83
332	Table II, column 2	1*	0·00694	0·00894
333	Table III, column 3	1*	386 hrs.	3856 hrs.
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346	Table I, column 3	1	$\psi \times 1000$	$\psi \times 1000$
,,	Do. Do	3*	17·1	19·2
349	eq. (*iv*)	5*	C_u	C_u
350		1*	about	above
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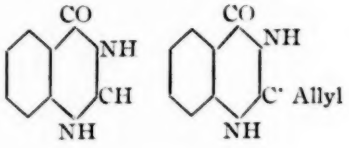
,,	Table V, column 3	3	0·264	0·274
396	Formula (I)			
408	Table V	1	199·6	169·6
547		4*	26·45%	29·45%
603		7	30%	3%
706		9	fixed	fixed;
707		10*	gold-platinum	gold-plated platinum
710		6*	change	exchange
713	Table II, compound 4		α-Dimethyl	Diphenyl
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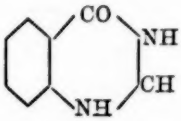
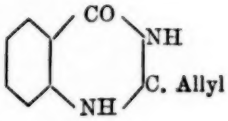
324	1	the gel etc.,	the hydrolysis of CCl_4 ceased. At this stage the gel, etc.
324	13	1190	100°
,,	14	0·304 m. moles	0·004 in moles
,,	Table II, column 1, line 2*	4·92	4·02
325	3, eq. (*i*)	CO	CO_2
327	6	35	36
328	Table I, column 3, line 1	H_2	H_2O
328	Do column 3 line 2*	9·05	0·05
,,	Do column 4 line 2	11·08%	11·68%
328	18*	$(C_1-C_2)-100$ log. g	$(C_1-C_2)/100$ g.
329	Table II, column 6, line 1	0·29	0·99
,,	Do line 2*	1·06	1·83
332	Table II, column 2, line 1*	0·00694	0·00894
333	Table III, column 3 line 1*	386 hrs.	3856 hrs.
,,	13*	03126 c.c.	0·3196 c.c.
,,	2*	0·0198	0·0123

* From bottom

ERRATA

Page	Line	*for*	*read*
337	12*	=0·474 c.c.	=0·774 c.c.
341	6*	1·0015 × 2·241	1·00851 × 2·241
346	Table I, column 3, line 1	$\psi \times 1000$	$\psi \times 100$
,,	Do column 3, line 3*	17·1	19·2
349	5* eq. (*iv*)	C_s	C_s
350	1*	about	above
354	12	m_a and m_b and	m_a and m_b are
,,	Table V, column 3, line 3	0·264	0·274
396	Formula (I)		
408	Table V.	196·6	169·6

* From bottom

ERRATA

Page	*line*	*for*	*Read*
22	2*	**CO**	CO_2
89	12	(*J. Indian Chem. Soc.*, **1933, 10,** 500.)	(*J. Indian Chem. Soc.*, **1930, 7,** 503).
171	Table II Column 2, line 3	0·5598g.	0·0550g.
	4	0·6673	0·0667g.
249	3	**Rosaniline hydrochloride**	*p*-**Rosaniline hydrochloride**
252	Table III	Do.	Do.

* From bottom.

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Potentiometric Estimation of Copper with Sodium Sulphide.

By C. Prasad and J. B. Jha.

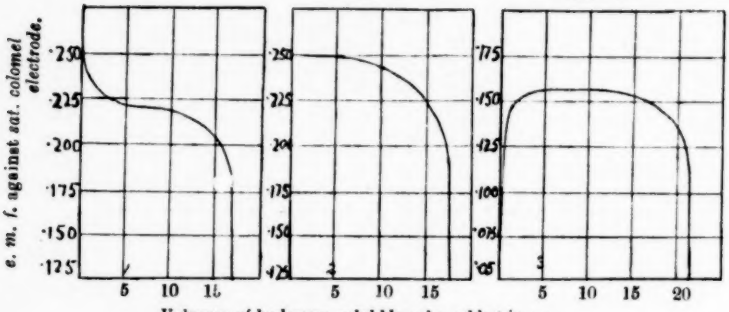
The possibility of the potentiometric estimation of copper with sodium sulphide has been shown by Jha (*J. Indian Chem. Soc.*, 1932, **10**, 41). The titrations were carried on with copper sulphate solutions containing a measured amount of acetic acid. It was also shown in the paper quoted above that for correct estimations the *regulation of the quantity of free acetic* acid is of considerable importance.

The titrations described in this paper were conducted with copper sulphate dissolved in buffer solutions with a view to (*i*) obviate the necessity of prejudging the amount of free acetic acid to be added to copper sulphate solutions, as required by the method already quoted, and to (*ii*) obtain complete titration curves under constant hydrogen ion concentrations as far as possible.

Experimental.

Copper in the form of copper sulphate was dissolved in buffer solutions. The hydrogen ion concentrations of the buffer solutions before dissolving the copper sulphate as well as afterwards, was determined electrometrically. There was very little difference in the hydrogen ion concentrations subsequently when copper sulphate was present.

FIG. 1. FIG. 2. FIG. 3.



Volumes of hydrogen sulphide soln. added in c.c.

Fig. 1. Vol. required to complete the titration 17·6 c.c., p_H 3·7
Fig. 2. ,, ,, ,, ,, 17·26 c.c., p_H 3·0
Fig. 3. ,, ,, ,, ,, 21·3 c.c , p_H 5·54
Titrations were done with $CuSO_4$ in $CH_3COONa - CH_3COOH$ buffer soln.

Sodium sulphide solution.—In order to get quantitative agreement between the precipitant and the copper sulphate to be titrated, sodium sulphide was freed from the sulphite, etc., by acidification and subsequent neutralisation (*loc. cit.*) till the solution was neutral to litmus. At this stage the solution contained mostly free hydrogen sulphide.

From the titration curves shown in Figs. 1-3, it is clear that upto a considerable distance from the beginning of the titrations there is no regularity in the *e.m. f.* variations which may take any form, although the compleeteness of the titrations is always marked with a sudden drop in potential. The potentials at the end point are found to rise with p_H as shown in Table I.

At present no explanation is available either to the irregularities observed in the *e.m.f* changes in the beginning or to the rise in the end-point potentials with p_H.

Some of the resuls of the titrations are shown in Table II. It will be seen that the most suitable range for making up the copper sulphate solutions is between p_H 3 to p_H 6. Above p_H 6, the error rises rapidly.

TABLE I.

p_H of the buffer in which $CuSO_4$ solns. were made	3·7	5·0	5·5	5·9	6·1
Average value of potentials at the end against sat. calomel electrode (volts)	0·063	0·07	0·083	0·097	0·100

TABLE II.

p_H	Strength of $CuSO_4$ soln.	Actual amount of $CuSO_4$, $5H_2O$.	$CuSO_4$, $5H_2O$ found by potentiometric titrations.	Error.
2·99	$M/121·26$	2·059 g./litre	2·059	0·0%
	$M/148·62$	1·680	1·685	0·3
3·73	$M/121·6$	2·059	2·065	0·3
	$M/148·62$	1·6800	1·672	0·6
4·30	$M/18·223$	13·702	13·728	0·2
	$M/29·160$	8·5800	8·576	0·2
5·0	$M/264·00$	0·9455	0·9500	0·5
	$M/312·60$	0·7987	0·8044	0·8
5·90	$M/183·92$	1·3580	0·3650	0·5
	$M/250·9$	0·9992	0·9995	0·03
6·09	$M/187·46$	1·332	1·348	1·2
6·11	$M/244·40$	1·022	1·045	2·25

SUMMARY.

1. The estimation of copper in the form of copper sulphate in sodium acetate acetic acid buffers can be carried on without adding any free acid. This obviates the judging of the proper amount of acid to be added before titrations. The best p_H range for the buffers to make up copper sulphate solutions is between 3—5.

2. The potentials at the end point have been found to rise with p_H.

Our thanks are due to Profs. H. Krall and B. L. Vaish for their interest in the work.

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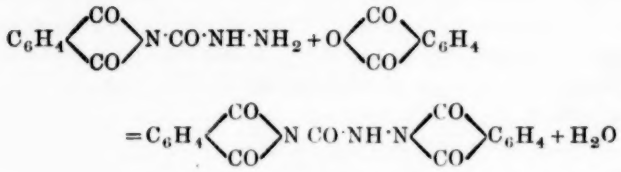
Studies in Acid Anhydrides. Action of Semicarbazides on Anhydrides of Dibasic Acids.

By B. K. Banerjee.

The action of *o*-diamines, benzidine, etc., upon anhydrides of dibasic acids has been studied by several authors (Chakravarti, *J. Indian Chem. Soc.*, 1924, **1**, 19, 330; Kollar, *Ber.*, 1904, **37**, 2880; Sircar, *J. Indian Chem. Soc.*, 1928, **5**, 397). The action of semicarbazide upon *o*-diketones, ketonic esters, etc., has also been studied (De, *J. Indian Chem. Soc.*, 1926, **3**, 33 ; De and Dutta, *ibid.*, 1928, **5**, 459 ; Bose, *ibid.*, 1924, **1**, 51 ; 1925, **2**, 95).

The action of semicarbazide on anhydrides of dibasic acids has been studied in this paper. Dunlap (*J. Amer. Chem. Soc.*, 1905, **27**, 1091) obtained phthalyl semicarbazide (m. p. 262°) by heating a mixture of equimolecular proportion of semicarbazide hydrochloride and phthalic anhydride at 160°. The same compound has been prepared by the author by a different method. The presence of the free amino group in phthalyl semicarbazide has been proved by condensing it with benzaldehyde, another molecule of phthalic anhydride and preparing an acetyl derivative.



In the case of camphoric and diphenic anhydrides, dicamphoryl and di-diphenic semicarbazides are obtained.

Experimental.

Phthalyl semicarbazide was prepared by refluxing an alcoholic solution of phthalic anhydride with an equimolecular quantity of semicarbazide hydrochloride dissolved in water for 1½ hours on the water-bath. The almost colourless crystals separated and when recrystallised from acetic acid melted at 260-61° (Dunlap, *loc. cit*, gives the m. p. 262°).

Benzylidenephthalyl semicarbazide.—Phthalyl semicarbazide (0·5 g.) was heated with benzaldehyde (0·5 c.c.) in an oil-bath with an air condenser for 15 minutes until a clear liquid was obtained. On cooling the mixture solidified and it was washed with alcohol and crystallised from alcohol as pale yellow needles, m. p. 170-71°. (Found: N, 13·73. $C_{16}H_{11}O_3N_3$ requires N, 14·33 per cent).

Triacetylphthalyl semicarbazide.—Phthalyl semicarbazide (0·5 g.) was refluxed with acetic anhydride (5 c.c.) for about an hour until it dissolved. Crystallised from dilute alcohol, it melts at 120-21°. (Found: N, 12·37. $C_{15}H_{14}O_5N_3$ requires N, 12·65 per cent).

Diphthalyl semicarbazide.—An intimate mixture of phthalyl semicarbazide and phthalic anhydride in equimolecular proportions and a little sodium acetate was heated on a sand-bath for 10 minutes. The fused mass was washed with hot water and the pale yellow solid was then extracted with alcohol several times. The residue was finally crystallised from acetic acid, m.p. 300° after softening at 295°. (Found: N, 11·7. $C_{17}H_{19}O_5N_3$ requires N, 12·53 per cent).

Dicamphoryl semicarbazide.—An intimate mixture of camphoric anhydride (2 mols.) and semicarbazide hydrochloride (1 mol.) and a little sodium acetate was heated on a sand-bath for an hour and the melt washed twice with hot water. It was crystallised from alcohol, m.p. above 300°. (Found: N, 9·7. $C_{21}H_{29}O_5N_3$ requires N, 10·42 per cent).

Di-diphenic semicarbazide.—A mixture of diphenic anhydride (0·5 g.) with semicarbazide hydrochloride (0·25 g.) and a little sodium acetate was heated on a sand-bath to fusion for 10 to 15 minutes. The sticky mass was then washed with water and the residue crystallised from dilute alcohol, m.p. 186-87°. (Found: N, 9·12. $C_{29}H_{17}O_5N_3$ requires N, 8·62 per cent).

Further work in this line is being continued.

My best thanks are due to Principal T. T. Williams and Prof. H. D. Mukherjea for their kind support and encouragement during the progress of this investigation.

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Received May 14, 1934.

A Note on the Determination of the Viscosities of Solutions by the Scarpa Method.

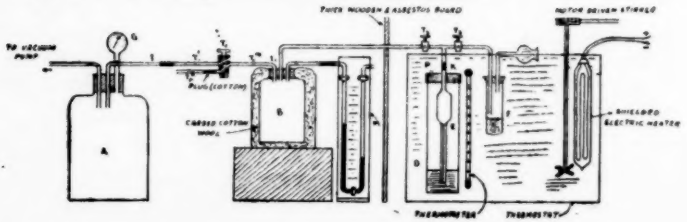
By B. K. Chatterji and B. L. Vaish.

Scarpa (*Gazzetta*, 1910, **40**, 271) devised a method for determining the viscosities of solutions without determining the densities. His viscometer consisted of a capillary 5-10 cm. in length and about 0·02 cm. in diameter. Bulbs of the capacities of 1 c.c., 5 c.c., 10 c.c., were blown in it and for any particular experiment any of the above bulbs were chosen. The capillary ended in a **U**-tube 30 cm. long and 2·0 cm. in diameter. The negative pressure to cause the flow of the liquid into the viscometer was produced by means of an aspirator whose pressure was well regulated. Times t_1 and t_2, required for filling and emptying the bulb under a known pressure, were noted. If V be the volume of the bulb, R the radius of the capillary and L its length, Scarpa deduced the formula, $\mu = \frac{\pi R^4}{8LV} \cdot P. \frac{t_1 t_2}{t_1 + t_2} = \text{Const.} \frac{t_1 t_2}{t_1 + t_2}$, if the same temperature and pressure be always employed. The value of the constant for a particular apparatus was determined by measuring t_1, $t_2/t_1 + t_2$ for a liquid, say water.

The method was later modified by Farrow (*J. Chem. Soc.*, 1912, **101**, 347) and recently by Joshi (*J. Indian Chem. Soc.*, 1933, **10**, 330) in his determination of viscosities of colloidal solutions.

The present authors attempted to find the viscosities of dilute solutions of strong electrolytes by the above method but all attempts failed to get reproducible results although the principles on which it is based were strictly adhered to.

The method is diagrammatically shown below.



Experimental.

The bottle A of 14 litres capacity is directly connected to a filter pump. The diminution in pressure in this bottle is shown by the gauge G. This was found very useful for adjusting the pressure in B and E.

The tube I is connected to I_1 and finally to B by glass tubing through the three-way tap II (used with vacuum grease). The part T''_1 of the tap is used to take in more air in case of the manometer M shows more negative pressure than is necessary, *i.e.*, the pressure in B is very accurately adjusted by means of the tap T_1 by turning it one way or the other.

The bottle B is enclosed in a glass beaker. The space in between the two is filled with cotton wool to shield the bottle from external changes of temperature. The diminution in pressure in B is shown by the manometer M.

The manometer.—This part of the apparatus was made as perfect as possible. Freshly distilled mercury which was washed with dilute nitric acid, water and finally with ether was used for the manometer. Other liquids were found unsuitable. A glass tube about a centimeter in diameter was thoroughly cleansed first with distilled water and then with caustic soda, subsequently with nitric acid and finally with distilled water again several times. It was then washed with alcohol and ether to remove the last traces of grease. It was then air-dried and bent to give the required form. The bore of the tube was uniform. This bent tube was filled with the above purified mercury. This was enclosed in two wider tubes. In one of the wider tubes was inserted a Beckmann glass scale just behind the arm of the manometer. The whole arrangement was made rigid by mounting it on a wooden board. The different tubes and scale, etc., were kept in position by means of corks and Golez wax. The meniscus of the mercury was read by means of a telescope. The Beckmann scale contained 29 divisions to a centimeter and with the help of the telescope it was possible to read it to a tenth of a division. The pressure difference was kept at 8 cm. of mercury. Hence the accuracy in this part of the apparatus was of the order of 1 in 2320 of a cm. This accuracy in the reading of the instrument was quite reproducible and sufficient for our purpose.

Construction of Viscometers.

Viscometer A was of the Ostwald type and was used first of all. Its dimensions are as follows:—

Diameter of the capillary = 0·2 mm., volume of the upper bulb = 10 c.c., length of the capillary = 5 cm.

This viscometer gave readings which were correct to about 1% as shown below. As our work required greater accuracy, the viscometer B was tried.

Viscometer B was of the type described by Joshi (*loc. cit.*). The volume of the upper bulb was greatly increased to increase the time of flow. The length of the capillary was also increased to prevent the formation of eddies. Before blowing the bulb the tubes were thoroughly cleansed to remove dust and grease. The following are the dimensions of the Scarpa tube:—

Length of the capillary = 16 cm., diameter of the capillary = 0·2 mm., volume of the bulb = 25 c.c.

The above Scarpa tube was fixed in a wider tube of $1\frac{1}{2}$ inches diameter by means of a tightly fitting rubber cap. Through this cap passed also a small thin tube of $\frac{1}{3}$ inch diameter and $\frac{1}{2}$ inch length to admit passage of air. The whole arrangement was fixed in the thermostat as shown in the diagram (E.D.).

As this viscometer was open to errors (*vide infra*) the following one was used.

Viscometer C was of the Ostwald type of the following dimensions. It was suspected that in the viscometer B the cause of error was unequal temperature effect as discussed afterwards.

Length of the capillary = 18 cm., diameter of the capillary = 0·2 mm., volume of the bulb = 47 c.c. The bulbs were blown from hard glass tubing cleaned thoroughly (as in the case of the manometer tubing) before blowing. This was then fixed in place of E. D. The other arm of the viscometer was plugged, through a side-tube by means of cotton wool to avoid dust.

Temperature control.—The temperature was controlled by immersing the viscometer in a thermostat of about 40 litres capacity, the temperature of which was controlled by a mercury-toluene regulator which worked through an electro-magnetic relay. The regulator was extremely sensitive and easily kept the temperature constant to a $\frac{1}{100}$ of a degree.

The water of the thermostat was heated electrically. The bath of the thermostat was kept at constant temperature at every place by means of a thoroughly efficient motor driven stirrer* with vanes just below the heater. The temperature of the thermostat was thus kept constant at every spot of the bath. The glow of the electric bulb (heater) was perfectly periodical when the thermostat was once set up and direct radiations from it, when glowing, to the viscometer was cut off by means of an iron cylindrical casing which surrounded the bulb. Under these circumstances no change of temperature was caused in the viscometer by the radiations from the glowing bulb.

Time measurements.—The time of the flow of the liquid up and down the capillary was read by means of a chronometer stop-watch which read to a fifth of a second. The times were reckoned from the instant the meniscus of the liquid crossed either of the viscometer marks. Although it was not possible to get a watch which could read to greater fraction of a second, it was not a very serious handicap considering the fact that the total time for the flow of the liquid in the viscometer was quite large, *i.e.*, of the order of 1000-3000 seconds. In order to read the meniscus accurately a $\frac{1}{2}$ C. P. lamp was fixed just behind the viscometer and at a distance (to eliminate temperature differences) and was switched on only for a fraction of a second just before the meniscus of the liquid crossed either of the marks of the viscometer.

Procedure.—First of all the bottle A was exhausted of its air content by means of a vacuum pump. The diminution in pressure was approximately indicated by the pressure gauge G, the three-way stop cocks T_1, T_2, T_3 being closed. The negative pressure in the system between T_1 and T_2 was then accurately adjusted by means of the stop-cock T_1 by rotating it one way or the other as necessary. This diminution in pressure was indicated accurately by means of the manometer M, the level of the mercury meniscus being read by means of a reading telescope, as described above. In all subsequent experiments the level was kept constant at this very level. Having adjusted the pressure in the apparatus some time was allowed to elapse so that the temperature differences caused by the change of pressure (adiabatic) might come to an equilibrium. The manometer was finally read again to see if any change took place during this period and if so a final adjustment was

* A blank experiment showed that the stirrer did not interfere with the viscometer readings. Special precautions were taken for this.

again made. The stop-cock T_2 was then opened and the stop-watch started. These two operations were done simultaneously because no time was taken by the liquid in D to rise and cross the viscometer mark. The air rushed in through the opening P. The stop-cock T_2 was then closed simultaneously with the stopping of the stop-watch when the liquid in the viscometer just crossed the upper mark. This was the time of rise. The stop-cock T_3 was then opened and when the meniscus of the liquid in the viscometer (now full) just crossed the upper mark, the stop-watch was started and was stopped when it just crossed the lower mark. With a little practice all this can be done with great regularity and precision. The same operation was repeated several times for the same liquid. For filling another liquid or solution the viscometer tube is detached from the apparatus at the joint K.

Every part of the apparatus was previously tested for leaks and was found leak-proof.

Reading with viscometer A.

Vol. of water (boiled and distilled water) = 10 c.c. Temp. = 25° ± 0·01.

No. of readings	...	1	2	3	4	5	6	7	8
Time for rise (sec.)	...	22·0	22·3	22·4	22·2	22·3	22·4	22·6	22·1
Time for fall (sec.)	...	33·0	32·8	32·6	32·6	32·6	32·6	32·8	32·6

These results show that there is no concurrency among the various readings. But in order to see whether the changes in time occur with solutions of electrolytes a molar solution of ammonium chloride was prepared and was put in the viscometer. The readings are as follows.

Viscometer A.

Vol. of 1·0*N*-NH_4Cl soln. = 10 c.c. Temp. = 25° ± ·01.

Time for rise (sec.)	...	24·0	24·1	23·6	23·4	23·6	23·8	23·4
Time for fall (sec.)	...	31·4	31·3	31·3	31·3	31·4	31·3	31·3

The actual viscosities are not calculated because of the observed *erraticity* in the times for rise.

It will be seen from the results that although the total times are different when compared to that required by water the concurrency of the results is wanting.

In general, in this viscometer 1 % error is usually comitted in the measurement of time. This is a serious error considering the aims of the work which requires an accuracy of at least 1 in 1000. The negative curvature in the viscosity concentration curves of strong electrolytes as pointed out by Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 2950) is in the region 0·2*N* to 0·002*N*. Hence it was thought proper to see whether the above viscometer would give a difference in the time of flow (in/out) for the dilute solution of strong electrolytes. The following are the experimental results.

Viscometer A'.

Vol. of water=10 c.c. Temp.=25°±·01. Pressure diff. kept constant at 2·25 cm. of Hg.

No. of readings	1	2	3	4	5	6	7	8	9	10
Time for rise (sec.)	21·7	22·0	22·3	22·0	22·1	22·2	21·6	22·4	21·8	22·0
Time for fall (sec.)	33·1	33·2	33·0	33·0	32·8	33·0	33·0	33·1	33·0	33·0

$N/10$-NH_4Cl=10 c.c. Temp.=25°±·01°. Pressure diff.=2·25 cm. of Hg.

No. of readings ...	1	2	3	4	5	6	7	8	9	10
Time for rise (sec.) ...	22·2	22·0	21·8	22·0	22·4	22·1	22·0	22·1	22·0	22·1
Time for fall (sec.) ...	33·0	33·2	33·1	33·0	33·1	33·3	33·1	33·0	33·0	33·1

$N/2$-NH_4Cl soln.

No. of readings ...	1	2	3	4	5	6	7	8	9
Time for rise (sec.) ...	22 7	22·7	22·6	22·4	22·3	22·6	22·4	22·7	22·5
Time for fall (sec.) ...	32·8	32·8	32·8	32·8	33·0	33·0	32·8	32·9	33·0

From the above it will be seen that the above viscometer fails to indicate difference in the time for rise or fall for even solution as strong as $N/10$. It is useless to take the mean of these readings, for the results in both cases are the same.

Viscometer B.

Pressure difference kept constant at 7·5 cm. of Hg.
Temp. 25°±·01. Volume of water in D=50 c.c. (Lot I).

Time for rise ...	18′ 2·6″	17′ 55·0″	18′ 3·0″	17′ 16·5″	17′ 26·0″	17′ 46·4″
Time for fall ...	61′ 11·0″	61′ 10·0″	61′ 9·0″	61′ 9·6″	61′ 9·4″	61′ 10·0″

Water Lot II. (From the same stock as in lot I).

Time of rise.	22′ 59·3″	22′ 34″	22′ 57·6″	23′ 3·2″	22′ 58·6″	22′ 56″	23′ 4·6″		
Time of fall.	62′ 15·3″	62′ 16″	62′ 15·8″	62′ 15·6″	62′ 15·8″	62′ 16″	62′ 15·6″		

Note:—In all the above cases only the final set of readings are given, each set of readings (given above and below) have been repeated several times.

From the above results it is obvious that the times of rise are absolutely erratic. The times for fall, however, are more or less concordant, at least they are satisfactory. From the erratic nature of the times, it was thought that the cause lay in (*i*) improper adjustment of pressure (negative) in B, (*ii*) unequal temperature in the various parts of the tube E.D., (*iii*) dissolution of glass by water or solutions, (*iv*) drying of the inner walls of the viscometer bulb E.

Any or all the above causes may be the reason for the observed discovery in the times of rise. A little reflection, however, shows that causes (*i*), (*iii*) and (*iv*) can easily be ruled out. The pressure adjustment was qu'te satisfactory in the sense that it read to 1 in 2000 and could not cause the observed erratic behaviour. Cause (*iii*) if it were operating at all, would have affected the times of fall as well. From the results it is apparent that it does not. The drying of the inner walls of the viscometer bulb cannot be the cause of the discrepancy because the air which enters the bulb during the flow out of the liquid is saturated with the vapours of the water (or test solution) kept in tube F. It appeared, therefore, that the main cause was (*ii*). This is apparent from the very construction of the viscometer B. In the first place, the outer jacket of the viscometer is in contact with the thromostat bath. Even though the whole arrangement was kept in the set thermostat for about an hour before taking the readings, it is no guarantee that inside the tube and above the level of the experimental solution, the temperature of the air and hence that of the viscometer bulb was the same as that of the thermostat. There is an air passage (P) in the cap of the viscometer outer tube and cold air (atmospheric temperature was 16°) would easily flow in thus causing an unequal distribution of temperature. It should also be noted that the volume of this cold air is not negligible because when the experimental solution (about 45 c.c.) is drawn up due to the negative pressure in B, an equal volume of cold air is drawn inside the wide tube D, thus causing temperature differences. This, however, does not affect the time for fall because once the viscometer bulb E is full of the

solution at 25° ± ·01, the temperature of the bulb may reasonably be expected to remain at that temperature and no appreciable fall of temperature may be expected during the flow out of the liquid from the viscometer bulb. Moreover, during this operation the cold air (drawing inside during the previous operation) is expelled out of E. This accounts for the constancy of the times for fall and the discrepancy in the times for rise. To eliminate this source of error, the viscometer C was constructed and used.

Viscometer C.—Temp. 25° ± ·01. Vol. of water (the water used was boiled distilled water, filtered through pure cotton wool to free it from any dust particles) = 50 c.c. Pressure diff. kept constant at 8 cm. of Hg.

Time for rise	... 24′ 20·0″	24′ 38·2″	24′ 23·3″	22′ 49·0″	24′ 5 4″
Time for fall	... 62′ 3·0″	62′ 3·6″	62′ 4·0″	62′ 3·6″	62′ 3·0″
Time for rise	... 24′ 19·8″	23′ 58·0″	23′ 58·0″	23′ 40·0″	
Time for fall	... 62′ 3·6″	62′ 3·6″	62′ 3·0″	62′ 3·4″	

Everything same as above. *N*/100-NaCl soln.

Time of rise	... 23′ 58·0″	23′ 34·0″	24′ 18·5″	24′ 36·8″	24′ 2·0″
Time for fall	... 62′ 45·48″	62′ 45·2″	62′ 46·0″	62′ 45·6″	62′ 45·8″

Discussion.

From the foregoing results it is seen that there is discrepancy between the various readings for the time of rise in all the three forms of the viscometer used. The possible causes of this discrepancy have been mentioned. The most plausible one seems to be the adjustment of pressure. But it has already been emphasised that great care was taken to eliminate this source of error. The authors have reasons to believe, considering the extent of accuracy attained in this direction, that this may not be the cause of the erratic results observed.

This degree of accuracy in the observation of pressure has not been obtained by any of the previous workers. Scarpa (*loc. cit.*) regulated the pressure by means of an aspirator by taking

out known volumes of water or by additions of it. The same principle was adopted by Farrow and by Joshi (*loc. cit.*). This method was also tested by the authors in a preliminary set of experiments and their results point to the conclusions that the method is not accurate. In the first place, it is not practicable to add or take out exactly the same amount of water each time so accurately as to maintain the constancy of pressure to a fraction of a mm. of Hg for all the observations. In the second place, the evaporation of the water in the aspirator under the diminished pressure causes disturbance which is bound to affect the maintenance of the constancy of the pressure. The authors are of opinion, however, that this method may be suitable where great accuracy in the measurement of viscosities are not required. Farrow determined the viscosities of soap solutions while Joshi used colloidal solutions for viscosity determinations. It is needless to add that in all these cases a high degree of accuracy is not required, at least not to the extent the present authors aimed at.

It has been pointed out by Jones and Talley (*J. Amer. Chem. Soc.*, 1933, **55**, 632) that "absolute cleanliness of viscometer is essential as a trace of dust or grease will give erratic results. Cleansing reagents can make as much trouble as the more obvious forms of dirt." In the above experiments perfectly pure substances were used even for cleaning and great pains were taken to avoid grease and dust. The viscometer was thoroughly washed several times with concentrated potash solution, then with chromic acid solutions (all these solutions were made with boiled distilled water). It was then washed several times with distilled water. The final washings were done with redistilled alcohol and pure ether and finally air-dried so that no possibility existed of some grease or dust particles interfering with the results. This is further confirmed by our observations which show good concordance of results so far as the time for fall is concerned.

Another point worth consideration is the velocity of flow (in or out) through the capillary of the viscometer. The Poisuelle law holds true only for steady and slow rate of flow. This was also kept in view in the above experiments. The negative pressure was so adjusted, by trial, that it was just slightly more than sufficient to lift the required volume of the test solution and no eddies or other disturbances were observed. As a matter of fact the viscometer C was constructed by trial, after many that were rejected on this account,

and the final one with 0·2 mm. diameter was chosen. Moreover the length of capillary was such that a very steady and slow rate of flow could be attained.

Incidently we come to the conclusion that the use of viscometer of the type B is open to serious error especially due to the temperature differences in its body. This has been discussed above. It was to avoid this source of error that the viscometer C was employed. In this case the whole body of the viscometer was directly in contact with the thermostat bath so that within experimental errors, at least this possible source of error was eliminated.

Jones and Talley (*loc. cit.*) have used a photo-electric cell to record the time automatically to avoid the errors arising out of the human factor. They, however, noted only the times of fall (in the Washburn Williams type of the viscometer). The above results show, however that under the conditions of the experiments this was not a source of error, at least, not to the extent of accounting for the observed erraticity of results for the time of rise.

The authors have tried to eliminate almost all the possible sources of error in the above series of experiments but yet it is puzzling to find the above-mentioned discrepancy in the times for rise while those for fall giving good readings.

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On a New Type of Liquid-Liquid Junction.

BY D. N. GHOSH.

The presence of liquid junction potentials is a source of considerable difficulty in the accurate measurement of the *e.m.f.* of cells. The use of a saturated solution of potassium chloride or ammonium nitrate as the bridge liquid (Bjerrum, *Z. physikal. Chem.*, 1905, **53**, 428; Cumming and Abbegg, *Z. Elektrochem.*, 1907, **13**, 17) does not always

completely eliminate the liquid junction potential (*cf.* Scatchard, *J. Amer. Chem. Soc.*, 1925 **47**, 696) whereas the method suggested by Bjerrum (*loc. cit.*) at best, eliminates the liquid potential only partially. Owing to their instability, the values of the junction potentials cannot be determined accurately by experimental methods. Weyl (Dissert. Karlsruhe, 1905), Lewis and Rupert (*J. Amer. Chem. Soc.*, 1911, **33**, 299), Cumming and Gilchrist (*Trans. Faraday Soc.*, 1913, **9**, 174) and various other investigators have attempted to get reproducible and constant junction potentials in order that their values might be determined. But in almost every case it has been found that the observed *e.m.f.* fails to give a constant value and changes by several millivolts through "ageing." These fluctuations in the values of the junction potentials are mainly due to disturbances produced by diffusion effects.

In order to minimise the disturbing effects of diffusion, various types of junctions have been attempted. Bjerrum (*Z. Elektrochem.*, 1911, **17**, 389) used finely divided sand as the medium where the two liquids were allowed to meet. Myers and Acree (*Amer. Chem. J.*, 1913, **50**, 396) and Lewis, Brighton and Sebastian (*J. Amer Chem. Soc*, 1917, **39**, 2245), have, however, shown that Bjerrum's method is not efficient. Lamb and Larson (*J. Amer. Chem. Soc.*, 1920, **42**, 299) sought to reduce diffusion by using finely bored capillary tubing, but as has been shown by Cumming and Gilchrist (*loc. cit.*) the procedure fails to give accurate values. Attempts towards decreasing the interfacial area of the junction by mechanical means such as plugging the ends of connecting tubes by rolls of filter paper, cotton wool or cones of wood and the use of glass taps without grease have all failed to give satisfactory reproducible values (*cf.* Glasstone, "Electrochemistry of solutions," p. 285).

Guggenheim (*J. Amer. Chem. Soc.*, 1930, **52**, 1315) has used a special type of liquid junction. The concentrations of the two solutions A and B, forming the liquid junction, were so adjusted that they gradually varied from 100% of A and 0% of B at one end to 100% of B and 0% of A at the other end. A continuous mixture junction of gradual concentration gradient was thereby obtained. Guggenheim considers such a bridge contact, superior to the free diffusion liquid junction. Recent investigation by Ferguson, Valentine and Hitchin (*J. Amer. Chem. Soc.*, 1932, **54**, 1279) have shown that the results with the types of junction used by Guggenheim

are not so satisfactory as those obtained by using a junction of the free diffusion type.

The flowing junction introduced by Lamb and Larson (*loc. cit.*) goes a long way towards giving reproducible junction potentials, where diffusion disturbances are considerably eliminated by constant renewal of the contact surface. Robert and Fenwick (*J. Amer. Chem. Soc.*, 1927, **49**, 2788) by using a special type of flowing junction have obtained values which are in accordance with the Lewis and Sargent formula. It has however, been shown recently by Ferguson (*loc. cit.*) that the potential of the flowing junction is dependent on the rate of flow and attains a constant value only when rate of the flow is rapid. Moreover, in the flowing junction, the two solutions are always in contact and this vitiates reproducibility as the potential difference is not restricted to the contact interface, but communicates to certain distance, within the bulk of the solutions in the half cells, as has been clearly demonstrated by Ferguson and co-workers (*loc. cit.*).

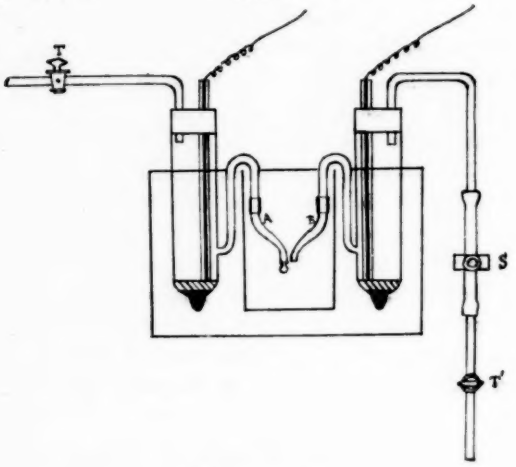
It is well known that the diffusion of a dissolved solid follows Fick's equation,

$$ds = -D.q.\frac{dc}{dx}.dt$$

where ds, the quantity diffused is directly proportional to q, the cross section, dt, the time and dc/dx, the concentration gradient. Most of the previous attempts summarised above have been directed towards minimising diffusion effects by a decrease of q, the interfacial area of the junction, whilst Guggenheim's constant mixture junction aims at lowering dc/dx, the concentration gradient at the contact interface. It is evident, however, that in addition to the above two factors a decrease in the value of dt, the time of contact of the two solutions forming the junction, should also contribute towards diminished diffusion. It was, therefore, hoped that by lowering the time of contact sufficiently, the ageing effect of the liquid junction would be largely eliminated. Keeping the above point in view, a type of junction has been devised where, in addition to a small interfacial area of the junction, the time of contact is reduced to a minimum by allowing the solutions to come in contact only momentarily. Using the junction described below, a series of determinations of the junction potentials have been

carried out and it has been found that it is capable of giving fairly constant and reproducible values.

FIG. 1.



EXPERIMENTAL.

The experimental arrangement is shown in Fig. 1. The cell was made up of two electrode vessels having no detachable side-tubes A and B. These were made out of thin walled glass tubings the bore of the tubings having a diameter of 1 mm. By manipulation of the tap T, a full grown drop was formed at the tip of A and kept suspended there. With the help of the capillary tap T′ and the screw-clip S, a drop could be gradually formed at the end of the tip B. The ends of the tips A and B were paraffined and the distance between them was so adjusted that the drop at the end of the tip B, when nearly fully formed, would come into contact with the drop previously suspended at the end of a tip A, and at the next instant both the drops would detach from the tips and fall down. Thus for the very short period the two drops were in contact, the electrical circuit was completed through the potentiometer, previously kept ready for measurement by depression of the X-key. By forming several pairs of drops by repetition of the above process, potentiometer could be easily made to give the exact value of the *e.m.f.* of the cell. It is important that both the drops detach immediately after they have come in contact with the another.

In order to test the reproducibility of *e.m.f.* of cells with the above type of junctions, a series of Hg | Hg_2Cl_2 and Ag | AgCl cells with different junction solutions were set up and their values measured. The materials employed for the setting up of these cells were very carefully purified. The calomel employed was prepared by the electrolytic method recommended by Hulett and Lipscombe (*J. Amer. Chem. Soc.*, 1916, **38**, 22). The silver chloride electrode was prepared according to the method of Carmody (*ibid.*, 1929, **51**, 2901). To exclude the action of light during measurements the Ag | AgCl cell was set up in electrode vessels which were coated with black Japan on the outside. The thermostat was run at 25° and the temperature was constant to $\pm 0{\cdot}02°$. The heater in the thermostat was screened to prevent any electrical leakage. The potentiometer used was a Tinsley one and was capable of giving readings to a hundreth of a millivolt. The experimental values are given in Table I.

TABLE I.

No.	Cell.	*e.m.f.* in millivolts. Observed with drop contact.		Obtained by previous authors.
1.	Hg | Hg_2Cl_2, 0·1*N*-KCl | 0·1*N*-HCl, Hg_2Cl_2 | Hg	28·16	27·8. 26·78.	Lewis Brighton and Sebastian Mc Innes and Yeh.
2.	Hg | Hg_2Cl_2, 0·01*N*-KCl | 0·01*N*-HCl, Hg_2Cl_2 | Hg	27·53	27·2.	L. B. and S.
3.	Hg | Hg_2Cl_2, | 0·0*N*-KCl ·01*N*-KCl, Hg_2Cl_2 | Hg	52·64	52·9.	Fales and Mudge
4.	Hg | Hg_2Cl_2, 0·1*N*-KCl | Sat. KCl, Hg_2Cl_2 | Hg	89·42	91·8	Do
5.	Hg | Hg_2Cl_2, 1·0*N*-KCl | Sat. KCl, Hg_2Cl_2 | Hg	37·96	38·7	Do
6.	Ag | AgCl, 0·1*N*-HCl | 0·01*N*-HCl, AgCl | Ag	91·80	92 37	Ferguson and co-workers
7.	Ag | AgCl, 0·05*N*-KCl | ·05*N*-KCl, AgCl | Ag	53·38	53·57	Mc. Innes and Parker
8.	Ag | AgCl, 0·1*N*-KCl | 0·01*N*-KCl, AgCl | Ag	53·24	54·00	Do
9.	Ag | AgCl, 0·1*N*-HCl | Sat. KCl, Hg_2Cl_2 | Hg	42·52	44·76	Ferguson and co-workers
10.	Ag | AgCl, 0·01*N*-HCl | Sat. KCl, Hg_2Cl_2 | Hg	96·60	99·16	Do

The reproducibility was observed in the above measurements to be within a few hundreth of a millivolt with the same setting but with different settings it rose to a few tenths. The values in the cells 1 and 2 involving a liquid junction potential between KCl/HCl are found to be distinctly higher than those given in literature,

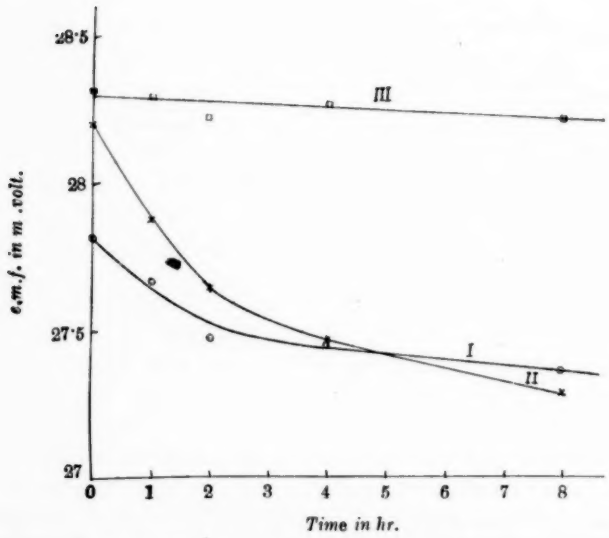
whereas the *e.m.f.* values of the concentration cells 3, 6, 7 and 8 are practically the same as given by previous investigators. It might be mentioned that the *e.m.f.* of concentration cells are independent of the nature of the liquid junction. The values with the saturated calomel electrodes as in cells 4, 5, 9 and 10 were, however, found to be somewhat lower than the values given in the literature.

It was desired to compare the variations with time of the values obtained with this drop contact method with those obtained on the same cell by the continuous mixture type of junction (*cf.* Guggenheim) and the free diffusion type (*cf.* Ferguson *loc. cit.*). The cell examined was

$$Hg \mid Hg_2Cl_2, 0{\cdot}1N\text{-}KCl \mid 0{\cdot}1N\text{-}HCl, Hg_2Cl_2 \mid Hg.$$

The continuous mixture was set up in N-tube filled with sand. For the free diffusion type of junction, a N-tube with a stop-cock (9 mm. bore) in the limb was used. The data obtained are given in Table II and the curves are plotted in Fig. 2.

FIG. 2.



I. Const. mixture type. II. From diff. type. III. Drop. contact technique.

TABLE II.

Time.	*e.m.f.* observed in millivolts with Free diffusion type. (*cf.* curve I)	Cont. mixture type. (*cf.* curve II)	Drop contact. (*cf.* curve III)
0	27·82	28·21	28·32
1 hr.	27·67	27·88	28·30
2	27·48	27·65	28·23
4	27·46	27·47	28·28
8	27·36	27·29	28·23

It is apparent from curve III in Fig. 2, that the characteristic initial fall in *e.m.f.* values is practically absent, whereas it is present in curves I and II. Incidentally it also proves the superiority of the free diffusion type of liquid junction over the continuous mixture type, agreeing with the observation of Ferguson and co-workers, as has been mentioned before.

TABLE III.

No.	Cell.	*e.m.f.* observed in millivolts by Free diffusion type.	Drop contact.	Difference in millivolts.
1.	Ag | AgCl, 0·1*N*-HCl | Sat. KCl, Hg_2Cl_2 | Hg	41·04	42·67	1·63
2.	Ag | AgCl, 0·01*N*-HCl | Sat. KCl, Hg_2Cl_2 | Hg	95·08	96·73	1·65

In Table III are given the *e.m.f.* values of two cells with calomel saturated KCl as one of their half cells, with the free diffusion and drop contact type of junctions. As there exists a definite difference of about 1·6 millivolt in both the cells between the two types of junctions, it is evident that saturated KCl solutions do not completely eliminate the liquid junction potentials as has also been observed by Scatchard (*loc. cit.*) and more recently by Ferguson and co-workers.

It is well known that there is a decrease in the *e. m. f.* of the 0·1*M* and 1*M*-KCl.calomel cells when used in conjunction with a saturated KCl bridge. Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 385) attributed this to the formation of a complex mercuric ion by the interaction of the alkali chloride and the calomel. But Fales and Mudge (*loc. cit.*) have definitely shown that this is due to the diffusion of the concentrated solution of KCl from the bridge

into the half cells. In the drop contact technique developed above, it is evident that the half cells are free from any such deteriorations. The ageing effect with time is also absent. Large quantities of cell liquids, as in the case of flowing junctions, are also unnecessary. The method may also be of great value in the case of *e. m. f.* measurements with colloidal solutions, where the bridge liquid often introduces further complications by coagulation of the colloids at the tips of the connecting tubes.

In conclusion, the author wishes to express his thanks to Dr. P. B. Ganguly, D.Sc. for his kind interest in this work.

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A Note on the Reduction of Selenium Dioxide by Carbon Monoxide.

BY EDWARD BARNES.

Carbon monoxide from formate was dried over P_2O_5 and freed from traces of oxygen by passing over red hot copper gauze and then granulated potassium hydroxide. Selenium dioxide was sublimed into the vessels (cleansed by chromic, nitric acid mixture) in a dry stream of oxygen with a little NO_2 (oxygen carrier). Carbon monoxide was then introduced by repeated evacuation. With sealed glass tubes no reduction had taken place after several days' exposure to tropical sunlight. With a quartz vessel no reduction was brought about by several hours' exposure to intense radiation from a quartz mercury lamp. By slowly heating sealed glass tubes in an electrical heater with a mica window slight reduction was observed to occur at about 250°. By careful heating, however, in a quartz vessel it was found that selenium dioxide could be sublimed unchanged in carbon monoxide. By continually subliming a quantity of selenium dioxide from one side of a vessel to the other in a stream of carbon monoxide by strong heating with a bare gas flame only 17·2 mg. of selenium was separated after 40 minutes and only 16 mg. of CO was collected in the absorption tube.

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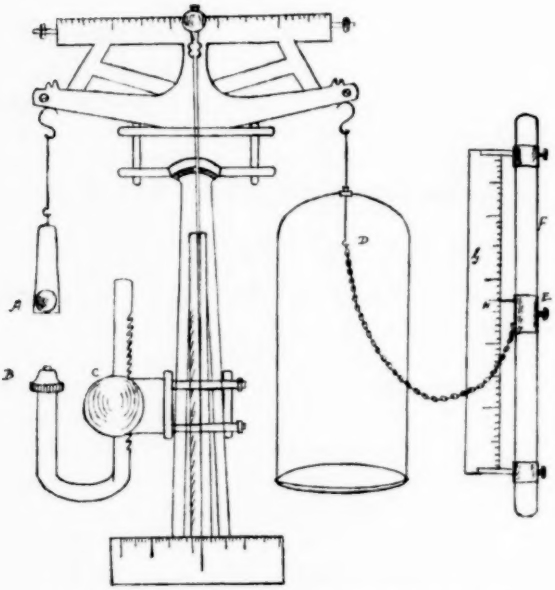
On the Tensile Strength of Jute-fibre.

By Pulin Behari Sarkar.

The fundamental defects for which jute is comparatively less important commercially are mainly its lack of durability and high lignin content. It is a well known fact that when exposed to dampness, the fibre loses much of its strength, the decaying process is supposed to be bacterial. Which component of the fibre is more susceptible to the attack of bacteria and how the process of deterioration goes on, are still unknown. In any case, this decomposition of the fibre has to be prevented in order to make it more useful for commercial purposes. Secondly, the presence of lignin makes the fibre tough and practically unfit for spinning. The light yellow colour due to lignin cannot be bleached by ordinary means. Thus lignin must be completely removed before it can be employed as a textile fibre just like cotton. But unfortunately all strength is lost with delignification, when the fibre is moist. Hence the removal of lignin while maintaining its strength is the real problem.

An attempt has been made here to study the factors on which the strength of the fibre actually depends, the conditions under which the deterioration takes place, as well as the effects of various chemical treatments on the tensile strength of the fibre before and after delignification. The tensile strength has been measured in an apparatus specially designed for the purpose. This consists of an ordinary balance in which the left pan has been replaced by two clips A and B. (A) is suspended from the left beam while (B) is attached to the balance pillar and can be moved up and down by rack and pinion arrangement (C). The right-hand beam carries a chain (D) the free end of which is attached to a siding clip (E) which is provided with a pointer and can be moved along a vertical glass rod (F). The chain helps to make delicate adjustments without causing any jerk. The weights thus added can be calculated from the scale (G) provided it is previously calibrated. The arrangement is shown below.



A. Upper clip. B. Lower clip C. Rack and pinion arrangement. D. Chain. E. Sliding clip. F. Vertical glass rod. G. Scale H. Pointer on sliding clip.

The fibre is rarely uniform in the true sense of the term, the diameter is never the same all through. The breaking weight being essentially dependent on the cross sectional area of the fibre, tensile strength was always measured with a fairly uniform fibre. The diameter was determined with a travelling microscope at different parts of the fibre and the mean was taken. At the same point however, the diameter is not always the same, the cross section being elliptical. So several readings were taken for the diameter at each point after turning the fibre, the mean giving the diameter of the fibre at that point. To avoid error in sampling only one or two fibres were selected from each stalk. The balance was adjusted by keeping the attached chain fixed at the lowest point. After carefully tightening the fibre, at both ends by A and B, C was very slowly turned to stress the fibre properly so that on releasing the pan the pointer remained at the zero position. The tightening of the fibre requires the greatest skill, if it be too tight at either end the fibre breaks there evidently with a lesser weight. When this took place the reading was discarded.

The weights must be very gradually increased, for it has been observed that a fibre not breaking with a greater weight, breaks with a smaller one if the latter be placed all at once. Several readings were taken with the same fibre and the mean accepted as the breaking weight. It has been noticed that with a certain weight the fibre does not break as soon as the pan is raised but only after a few seconds. Even with all possible precautions the results were seldom coincident. Twenty five observations were therefore taken in each case, the mean representing the tensile strength. In the same sample a few fibres were found to be abnormally strong, while a few others subnormally weak; these were discarded while taking the mean. The tensile strength was calculated from the formula:—

$$T = \frac{W}{\pi(d/2)^2}$$

The weight w was expressed in kg. and the diameter in mm.

Deterioration of Jute-fibre with Time.

In order to see how the fibre deteriorates with time, the tensile strength of a two years old sample of jute kept in a cupboard was measured. Green jute plant was retted in the laboratory and the tensile strength of the fresh fibre obtained therefrom was then determined. The difference was inappreciable. Thus the statement "even under ordinary conditions the (jute) fibre becomes brittle and loses much of its strength" (Mathews, "Textile Fibres," 1924, p. 768) is not substantially correct. When exposed to dampness the case is of course different. Unlike cotton, jute fibre showed a slight decrease in tensile strength with increasing humidity and *vice versa*. The results are shown in Table I.

TABLE I.

Specification of jute.	Moisture.	Mean tensile strength.	Standard error.
(*a*) Fresh fibre obtained by retting, air-dried.	14·80 %	15·61 kg./sq.mm.	± 1·50
(*b*) Raw jute kept for two years in the cupboard.	14·20	14·46	± 1·46
(*c*) Sample (*b*) dehydrated in a drying pistol over P_2O_5 in vacuum.	Nil	18·24	± 1·49
(*d*) Sample (*b*) kept under distilled water for 48 hours	...	12·81	± 1·51

Influence of Different Constituents on the Strength of the Fibre.

The influence of the different constituents on the tensile strength was next studied. Fatty and resinous matter was removed by extraction with a boiling mixture of alcohol and benzene (1 : 1) in a soxhlet apparatus for 5 to 6 hours. The two years old sample was always taken for investigation. The tensile strength remained practically unchanged after the removal of fats and resins. Lignin was removed completely by chlorine peroxide gas in presence of moisture. The milk-white fibre dissolved to a colourless solution in 72% H_2SO_4 in the cold. The delignified fibre retained its physical structure as seen under the microscope. The tensile strength in the air-dried condition was very nearly the same. This unmistakably indicates that in jute, lignin is not chemically combined with cellulose, otherwise these important physical properties of the fibre would have changed. This has also been observed by Chowdhury and Paul (unpublished paper) in the case of cocoanut fibre. Wislicenus (*Z. Chem. und Kolloid*, 1910, **6**, 17, 87), König (*Chem. Z.*, 1912, **36**, 1101) and Lehne and Shepmann (*Z. angew. Chem.*, 1925, **38**, 93) from the study of other lignocellulose also arrived at the same conclusion. The delignified fibre is very flexible and soft to the touch. But unfortunately, the tensile strenth while moist, is almost nil—it breaks with any weight however small if the fibre be kept moist with a brush during measurement. Otherwise it dries partly and a moderate value for tensile strength is obtained. Hemicelluloses therefore appear to be the real binding material and not lgnin as is usually supposed. Lignin serves more or less as a protective coating. Pectin was then removed from the delignified jute by extraction with 0·5% solution of ammonium oxalate at 80°-90° exhaustively. The tensile strength was found to be a bit lower. The samples were all air-dried and measurements were made in the same week, so the moisture content was not determined. Table II gives the experimental results.

TABLE II.

Specification of jute.	Mean tensile strength.	Standard error.
(*a*) Raw jute after removal of resin and fat	14·30	± 1·50
(*b*) Delignified jute, air-dried	15·32	± 1·48
(*c*) Do moist	10·86	± 2·0
(*d*) Do moistened with a brush during measurement	Nil	—
(*e*) Delignified jute after removal of pectin	14·72	± 1·38

Influence of Dampness on Jute-fibre.

The rate at which the fibre loses its strength when exposed to dampness was then determined. Raw jute was kept under tank water in a porcelain vessel and tensile strength was measured from time to time. It will be seen from Table III that the deterioration is not so rapid as is usually observed when the fibre is in contact with the soil. This might be due to the action of bacteria coming thereform as well as the nitrogenous matter present therein. The colour became darker with time and the fibre harsh to the touch. It is interesting to note here that the portion of the fibre above the water surface was very much weaker (as tested by the hand) than that under water.

TABLE III.

Sample—Raw jute.

Time.	Mean tensile strength.	Standard error.	Colour.
Nil	14·46	±1·46	ery pale brown
30 days	13·88	±1·47	,, ,,
60	12·16	±1·48	Light grey
90	11·31	±1·47	,, ,,
120	10·87	±1·49	Grey
150	10·02	±1·51	Dark grey

Prevention of Deterioration of Fibre.

In order to prevent the deterioration of the fibre it was treated in the cold with a 40 % solution of formaldehyde for 48 hours. The fibre was thoroughly washed, dried in air and its tensile strength measured. The value was, however, found to be almost double the original. With delignified fibre as well, the same rise was observed, but not in the moist condition. Jute was treated with cold and dilute NaOH for the same period, the tensile strength increased much in this case also. Alkaline formaldehyde was more efficient than acid solution in improving the tensile strength. Phenol and formaldehyde had the same influence as formaldehyde alone. The colour turned brown after alkali treatment, but remained unchanged

in acid and neutral formaldehyde treatment. In the former case the fibre became softer. In the case of mixed treatment the ratio was always 1:1.

TABLE IV.

Treatment.	Mean tensile strength.	Standard error.	Colour. Light	brown.
(1) Raw jute (air-dried)	14·46	±1.46	,,	,,
(2) Do with 40% H·CHO	26·37	—	,,	,,
(3) ,, ,, 10% ,,	25·46	—	,,	,,
(4) ,, ,, 10% CH_3COOH	13·82	—	,,	,,
(5) ,, ,, 8% NaOH	33·17	±1·61	Pale	brown
(6) ,, ,, 1% NaOH	33·77	—	,,	,,
(7) ,, ,, 10% acetic acid and 10% formaldehyde	31·39	—	Unchanged	
(8) With 4%NaOH and 10% H·CHO	42·0	±2·08	Brown	
(9) ,, 1% NaOH and 10% H·CHO	40 43	—	,,	
(10) 10% H·CHO and 10% phenol	27·0	±1·92	Unchanged	
(11) ,, 10% H·CHO and normal H_2SO_4	23·80	—	,,	
(12) Delignified jute	15·32	—	White	
(13) Do with 10% H·CHO	26·45	±2·10	,,	
(14) ,, 10% H·CHO and 1% NaOH	40·15	—	Pale	yellow
(15) ,, 1% NaOH alone	32·80	±1·93	,,	,,

Bacterial Decomposition of Jute-fibre.

Bacterial decomposition of jute, both treated and untreated was next studied. Green jute plant was retted in a porcelain vessel and the fibre under examination was dipped in it. The bacteria present in the over-retted jute hastened the process of deterioration. It is interesting to note here that in a galvanised iron vessel jute did not ret even in three months in stagnant water. Metallic zinc has therefore a distinct inhibiting action on the retting of jute. The tensile strength was measured every week. From the results given in Table V it is evident that raw jute is more resistant than delignified jute, showing thereby the protective nature of lignin.

Formaldehyde treated jute (raw) practically withstands all bacterial attack while delignified jute similarly treated undergoes slight deterioration. Formaldehyde, therefore, can be employed as a valuable bactericide in the case of jute to increase its durability.

TABLE V.

Mean tensile strength of

Time.	Raw jute.	Raw jute and H·CHO.	Delignified. jute.	Delignlfied jute and H·CHO.
Nil.	14·46	26·37	15·32	26·45
7 days	14·02	26·08	13·75	26·06
14	13·68	26·03	12·76	25·56
21	13·00	26·01	11·60	25·40
28	12·46	25·80	10·52	25·00
35	11·71	25·53	9·45	24·67
42	11·00	25·52	8 50	24·08
49	10·02	25·00	7·00	23·80
56	9·30	24·87	5·70	23·32
63	9·00	24·80	4 34	22·88

All attempts to maintain the strength of the delignified fibre in the moist condition have so far proved futile. Formaldehyde alone and with various other chemicals were found to be ineffective. Further work in this direction is in progress.

SUMMARY.

1. The tensile strength of jute fibre after various treatments has been measured by an apparatus specially designed for the purpose.

2. With increasing moisture the tensile strength diminishes and *vice versa*.

3. Deterioration with time is very negligible if the jute be kept in a dry place.

4. The maintenance of strength and structure by delignified jute supports the view that in jute, lignin and celluiose are not chemically combined.

5. Formaldehyde increases the tensile strength of the fibre specially in slightly alkaline solution. It also prevents the bacterial decomposition of both raw and delignified fibre.

6. Removal of lignin makes the fibre more susceptible to bacterial action.

I wish to record here my sincere and grateful thanks to my teacher Dr. J. K. Chowdhury, Ph.D., for designing the apparatus and many valuable suggestions, and to Prof. Dr. J. C. Ghosh for offering me all facilities for work.

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Vitamin C in Indian Food-stuffs.

BY A. R. GHOSH AND B. C. GUHA.

Since the identification of vitamin C (ascorbic acid) with "Hexuronic acid" additional interest has naturally been aroused in obtaining further information about it. The reducing property of ascorbic acid has been taken advantage of for the determination of the ascorbic acid content of different materials, both of vegetable and animal origins. The Tillmans technique of titration with the oxidation-reduction indicator, 2:6-dichlorophenol-indophenol, has been modified by Harris and Ray (*Biochem. J.*, 1933, **27**, 303) and Birch, Harris and Ray (*ibid.*, 1933, **27**, 590) and they claim that in general the figures obtained by the chemical method agree with those obtained by the biological technique of assay.

The present paper records certain results obtained by the titration technique with the extracts of some Indian food-stuffs and it will be observed that some of the fruits investigated have a very high reducing power. The vitamin C content of germinated and ungerminated *mung* (*Phaseolus mungo*) has been investigated by both the chemical and biological methods.

EXPERIMENTAL.

Titration with 2:6-dichlorophenol-indophenol.—Essentially the method of Harris and Ray (*loc. cit.*), and Birch, Harris and Ray

(*loc. cit.*) was followed. It has already been reported (Guha and Ghosh, *Current Science*, 1934, **2**, 390) that the dye is decolorised by itself in the presence of trichloroacetic acid. The velocity of reduction by ascorbic acid is, however, so rapid that in most cases this spontaneous decolorisation by trichloroacetic acid introduces no perceptible error. In the cases of trichloroacetic acid extracts containing very small amounts of ascorbic acid, however, where the time taken for titration exceeds 1-2 minutes, an appreciable error may be introduced. We have, therefore, in all our estimates added 1 c.c. of glacial acetic acid to 0·05 c.c. of 0·01*M*-dye in order to inhibit the spontaneous decolorisation, before titration against the trichloroacetic acid extracts (Guha and Ghosh, *loc. cit.*). We have lately found that Bessey and King(*J.Biol. Chem.*, 1933, **103**, 687) have used hot acetic acid extracts in many cases with the same purpose. We had ourselves tried extraction with cold glacial acetic acid but the centrifugate was opalescent and the extraction not so satisfactory as with trichloroacetic acid. After the end of titration, a faint pink colour persists very frequently, but with a little experience any error from this source may be obviated.

Titration with iodine.—Titrations of the trichloroacetic acid extracts have also been carried out with 0·01*N*-iodine. The results obtained by this method are, as might be expected, at variance with those obtained by titration with the indophenol indicator. The two values agree, however, for lemon juice, as has already been pointed out by Bessey and King (*loc. cit.*). In lemon juice, therefore, the amount of reducing substances other than the one reacting specifically with the indophenol indicator must be small.

In Table I are given the titration values of trichloroacetic acid extracts of the food-stuffs with 0·01 *N*-iodine and 0·01*M*-2:6-dichlorophenol-indophenol. The values of ascorbic acid have been estimated on the assumption that the sole reducing substance of the extracts, reacting with either reagent, is ascorbic acid. Two series of values have thus been obtained, and as will be seen, the only agreement is in the case of lemon juice (Bessey and King, *loc. cit.*). This is as might be expected, as usually there are reducing substances present, which react with iodine but not with the dye under our conditions of titration. The figures for ascorbic acid, given in the last column and computed on the assumption of the relative specificity of the method of titration with the indophenol dye are, therefore, held to be more reliable. There is substantial

(Harris and Ray, *Biochem. J.*, 1933, 27, 580) but not conclusive, evidence for this view.

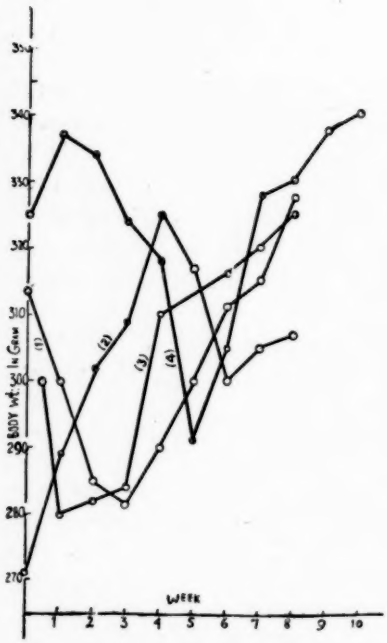
1 C.c. of the dye solution and 1 c.c. of the iodine solution were equivalent to 1·04 mg. and 0·88 mg. of ascorbic acid respectively.

The food-stuffs investigated are all fruits, except No. 8, 11, 17, 18, 22 and 26, which are vegetables and No. 15, which is a pulse. In Table II the ascorbic acid values of the richest Indian fruits are given.

The Vitamin C Values of Germinated and Ungerminated Kanchamung (*Phaseolus mungo*).

Kanchamung was germinated by being soaked with water for 48 hours covered with a piece of moist muslin in a procelian dish.

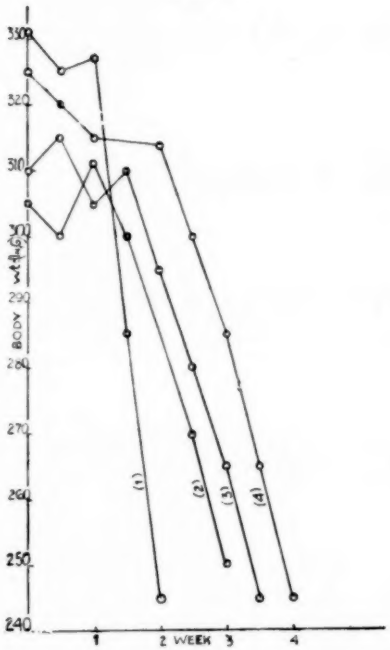
FIG. 1.



Curves obtained on administering 4 g. germinated mung daily. No scorbutic symptoms noticed during a 63 day expt. period.

The vitamin C values of germinated and ungerminated *mung* were estimated by both the biological and titration methods. The biological tests were carried out by the protective technique. Guinea-pigs, weighing about 300 g., were fed on a basal diet, consisting of 70 part oats, 20 parts crushed gram, 10 parts bran and 1 part cod-liver oil. A block of rock salt was also provided in each case. Those receiving this diet alone rapidly declined in weight and died within 2-3 weeks with typical scorbutic symptoms. The potency of the *mung* was tested by observing whether protection would be afforded for a 63-day period by graded doses of the food-stuff.

FIG. 2.



The curves obtained on administering 12 g. ungerminated *mung* daily. All the animals succumbed within 4 weeks.

Figs. 1 and 2 show that 4 g. of germinated *mung* daily are able to afford protection (*cf.* Wats and Eyles, *Indian J. Med. Res.*, 1932, **20**, 89) but even 12 g. of ungerminated *mung* daily are quite neffective. 3 G. of germinated *mung* were found to be just insufficient to prevent scurvy. This would show that, calculated on the basis of fresh weight, more than 4 times ascorbic acid is produced in *mung* by germination, as determined biologically. It will, however, be seen from Table I (serial No. 15) that on the basis of fresh weights, the ascorbic acid content, as estimated by titration with the indophenol indicator, is 0·04 mg. per g. in both the germinated and ungerminated *mung*. (As, however, the germinated and ungerminated *mung* contain 65·4 and 8·4% water respectively, there is about 7·8 times increases in vitamin C produced by germination, calculated on the basis of dry weight). Johnson (*Biochem. J.*, 1933, **27**, 1942) states that germinated peas contain a substance in addition to ascorbic acid, which reduces the indophenol reagent and that trichloroacetic acid does not extract all of the ascorbic acid of germinated peas. In our experiments also the titrimetric value of the trichloroacetic acid extract does not appear to agree well with the high biological value of the fresh germinated *mung*. Its protective dose is 4 g., whereas titrimetrically only 0·16 mg. ascorbic acid appears to be present in the trichloroacetic acid extract of this quantity of germinated *mung*.

TABLE I.

Serial No.	Bengali names.	English names.	Scientific names.	Values per g. of fresh food stuff. I_2—values (0·01 *N*).	Ascorbic acid(?) as calculated from iodine values.	Indicator (0·01 *M*).	Ascorbic acid as calculated from dye values.
1 (*i*)	Am, (Bengali deshi variety)* (Kancha).	Mango (green)	Mangifera indica	0·83 c.c.	0·73 mg.	0·2 c.c.	0·22 mg.
(*ii*)	,, (Bengali deshi variety)* (Paka).	(ripe)	,,	0·18	0·16	0·1	0 10
(*iii*)	,, Fozli variety	(ripe)	,,	0·5	0·44	0·33	0·34
(*iv*)	,, Langra variety	(ripe)	,,	1·0	0·88	0·66	0·69
(*v*)	,, (Bengali deshi variety)@						
	(*a*) Mukul	(bud)	,,	0·41	0·36	0·099	0·10
	(*b*) Kancha	(green)	,,	0·11	0·097	0·051	0·05
	(*c*) Paka	(ripe)	,,	0·05	0·044	0·02	0·02
2	Ānārash (Bengali deshi variety).	Pine-apple	Ananas sativa	0·31	0·27	0·21	0·22
	,, (Singapore)	,,	,,	0·26	0·23	0·07	0·07
	,, Canned (Malay)	,,	,,	0·14	0·12	0·099	0·11
3	Begoon (Blue variety)		Solenum melongena	0·09	0·079	0·05	0·05
	,, (White variety)		,,	0·12	0·11	0·05	0·05
4	Bel (Paka)	Wood-apple	Aegle marmelos	0·38	0·33	0·17	0·18
5	Dalim	Pomegranate	Punica granatum	0·20	0·18	0·11	0·11
6			Cucimis melo	0·06	0·053	0·03	0·03
7	Golap-jam	Rose-apple	Eugenia jambos	0·14	0·12	0·06	0·06
8	Hinche		Enhydra fluctuans	0·08	0·07	0·03	0·03
9	Jamrool		Eugenia malaccensis	0·09	0·079	0·04	0·04
10	Kala jam	Indian black-berries	Eugenia jambolana	0·28	0·25	0·15	0·16
11	Kalmi-shak		Ipomoea reptans	0·08	0·07	0·06	0·06
12	Kamala-lebu*	Orange	Citrus aurantium	0·27	0·24	0·17	0·18
13	Kamranga	Carambola	Averrhoa carambola	0·12	0·11	0·22	0·23

* The values are given per c.c. of the pulp.
@ Belonging to one particular tree.

TABLE I (*Contd.*).

Serial No.	Bengali names.	English names.	Scientific names.	Values per g. of fresh food stuff. I_2—value (0·01 *N*).	Ascorbic acid ? as calculated from iodine values.	Indicator (0·01 *M*).	Ascorbic acid as calculated from dye values.
14	Kanchalanka (Bombai)	Chillies	Capsicum indicum	0·09 c.c.	0·079 mg.	0·04 c.c.	0·04 mg.
	,, (Maldah)	,,	,,	2·3	2·02	0·43	0·45
	,, (Patna)	,,	,,	0·34	0·3	0·099	0·1
15	Kanchamug (germinated)	...	Phaseolus mungo	0·15	0·13	0·04	0·04
	,, (ungerminated)	...	,,	0·14	0·12	0·04	0·04
16	Kumra	...	Cucurbita maxima	0·12	0·11	0·05	0·05
17	Kumra-shak	...	Leaves of Cucurbita maxima.	0·27	0·24	0·11	0·11
18	Lau-shak	...	Leaves of Lagenaria vulgaris.	0·14	0·12	0·05	0·05
19	Lebu	Lemon	Citrus medica	0·23	0·2	0·18	0·19
20	Lichoo	Lichi	Nephelium lichi	0·9	0·79	0·46	0·48
21	Nonaphal	Bastard apple	Anona reticulata	0·44	0·39	0·14	0·15
22	Palang-shak	...	Spinach oleracea	0·08	0·07	0·06	0·06
23	Paniphal	...	Trapa bispinosa	0·2	0·18	0·14	0·15
24	Papaya	Papaw	Carica papaya	0·36	0·32	0·18	0·19
25	Peara	Guava	Psidium gujava	1·67	1·47	1·0	1·04
26	Pooin-shak	...	Basscla cordifolia	0·17	0·15	0·08	0·08
27	Sasha	Cucumber	Cucumis sativus	0·06	0·53	0·04	0·04
28	Sobeda	Sapota	Achras sapota	0·03	0·026	0·06	0·06
29	Tal-sansh	Core of the unripe fruit of the palm	Borassus flabellifer	0·08	0·07	0·04	0·04
30	Tarmuj	Water-melon	Citrullus vulgaris	0·13	0·11	0·07	0·07
31	Uchche	...	Momordica Charantia	0·52	0·46	0·32	0·33

TABLE II.

Serial No.	Bengali names.	English names.	Scientific names.	Ascorbic acid (mg.) as calculated from dye values per g. of fresh food-stuff.
1	Peara	Guava	Psidium gujava	1·04 mg.
2	Am (*Langra*)	Mango	Mangifera Indica	0·69
3	Lichoo	Lichi	Nephelium lichi	0·48
4	Kancha lanka (Maldah)	Chilli	Capsicum Indicum	0·45
5	Am (*Fozli*)	Mango	Mangifera Indica	0·34
6	Uchche	...	Momordica Charantia	0·33
7	Kamranga	Carambola	Averrhoe Carambola	0·23
8	Ānārash (Indian variety)	Pine-apple	Ananas Sativa	0·22
9	Lebu	Lemon	Citrus medica	0·19
10	Papaya	Papaw	Carica papaya	0·19
11	Bel (Paka)	Wood-apple	Aegle Marmelos	0·18
12	Kamala-lebu	Orange	Citrus Aurantium	0·18

SUMMARY.

1. Ascorbic acid in the trichloroacetic acid extracts of food-stuffs has been estimated by titration with 2:6-dichlorophenol-indophenol. Glacial acetic acid was introduced to inhibit to some extent the decolorisation by trichloroacetic acid itself.

2. The mango of a particular tree was investigated at the bud, unripe and ripe stages and a progressive decrease in ascorbic acid content was observed. It would seem, therefore, that the process of development of the fruit, unlike that of germination of the seed, involves a progressive disappearance of ascorbic acid.*

3. Of the various Indian food-stuffs investigated, the guava, the mango (*langra* variety) and the lichi appear to be the richest sources of vitamin C. They are richer than the Indian orange and lemon. The different varieties of the mango differ markedly in their ascorbic acid content (*cf.* Guha and Chakravorty, *Indian J. Med. Res.*, 1933, 20, 1045),

4. Germination increases the ascorbic acid content of *mung* 7·8 times, as calculated on the basis of dry weight. There is indication that trichloroacetic acid does not completely extract the vitamin C of germinated *mung*.

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* The same phenomenon has been observed with the guava of a particular tree, investigated at the bud and unripe stages (Guha and Ghosh, *Current Science*, 1934, 3, 201).

The Alkaloids of *Rauwolfia Serpentina*, Benth. Part II. Studies in the Ajmaline Series.

By Salimuzzaman Siddiqui and Rafat Hussain Siddiqui.

In the course of a discussion (Part I, *J. Indian Chem. Soc.*, 1932, **9**, 539) on the identity of rauwolfine, $C_{21}H_{26}O_2N_2$, m.p. about 160°, isolated from *Rauwolfia serpentina* by van Itallie and Steenhauer, (*Arch. Phar.*, 1932, **270**, 313) with ajmaline, $C_{20}H_{26}O_2N_2$, m. p. 158-60° (*J. Indian Chem. Soc.*, 1931, **8**, 667), the authors had noted the presence of N-Me and NH in ajmaline as forming an unaccountable contrast to rauwolfine, but admitted the possibility of the Dutch authors' formula for it, as there was evidence to show that ajmaline is not completely dehydrated at 100° and its analysis reported after dehydration at that temperature could also correspond to $C_{21}H_{26}O_2N_2$, $\frac{1}{2}H_2O$. A series of combustions, however, carried out since and controlled through microanalysis (particularly after complete dehydration at 200°, (*cf.* chart below) as well as the results of studies in the mutual relationship of ajmaline and its subsidiary alkaloids, lead the authors to the conclusion that original formula for ajmaline $C_{20}H_{26}O_2N_2$ should be retained.

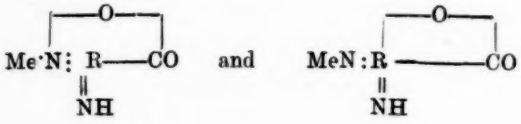
Ajmaline			C.	H.	N.
			73·10	8·13*	8·40*
After drying to const. wt. at 150°	...	Found	73·00	7·84*	8·52*
After heating at 200°	...	Found	73·80	7·89*	8·56*
$C_{20}H_{26}O_2N_2$	...	Req.	73·60	8·00	8·60
$C_{21}H_{26}O_2N_2$	...	Req.	74·55	7·69	8·22
After drying at 100°	...	Found	72·80	7·70	
			73·03	8·12	
			72·30	8·13*	8·40*
$C_{20}H_{26}O_2N_2 + \frac{1}{2}H_2O$	...	Req.	72·61	7·70	8·10
$C_{21}H_{26}O_2N_2 + \frac{1}{2}H_2O$	...	Req.	72·62	7·70	8·75
After long exposure to air	...	Found	67·00	8·30	7·62
$C_{20}H_{26}O_2N_2 + 1\frac{1}{2}H_2O$	...	Req.	66·86	7·91	8·21

The CH values noted for nitrosoajmaline in Part I (*loc. cit.*), agree much better with the C_{20}-formula (the N values being good for both). (Found: C, 67·7; H, 7·11, N, 11·5. $C_{20}H_{26}O_2N_2 \cdot NO$ requires C, 67·6; H, 7·00; N, 11·8; and $C_{21}H_{26}O_2N_2 \cdot NO$ requires C, 68·67; H, 6·91; N, 11·41 per cent). Also the C, H values for benzoylajmaline

* Indicates the values of microanalysis by Dr. Ing. A. Schoeller, Berlin.

(*loc. cit.*) tally more closely with the C_{20}-formula. (Found: C, 74·6, 74·5; H, 8·05, 8·09. $C_{20}H_{26}O_2N_2{\cdot}CO{\cdot}C_6H_5$ requires C, 75·4; H, 7·00; and $C_{21}H_{28}O_2N_2{\cdot}CO{\cdot}C_6H_5$ requires C, 75·8; H, 7·00 per cent).

It has been further shown that ajmaline takes up 2 atoms of bromine in the cold yielding a crystalline dibromo derivative, which indicates the presence of an olefine double bond in its molecule. It also forms a sulphonic acid, characterised through its salts, and a trinitro derivative. From the crystalline product obtained on heating ajmaline to 200° (*loc. cit.*), and provisionally named in its crude and undefined condition as pyroajmaline (shrinks 240°, m. p. 256°) it has been possible to isolate after repeated crystallisation from ethyl acetate some unchanged ajmaline (m. p. 158-60°) but mainly a product which melts at 265-66°, agreeing with ajmaline in its analysis, colour reactions and NH and N-Me groups, but differing from it in being diacidic in character. It thus appears that ajmaline crystallises from moist ethyl acetate with three molecules of water (*vide* H_2O value in freshly prepared and air-dried ajmaline, *J. Indian Chem. Soc.*, 1932, **9**, 539), of which it loses $1\frac{1}{2}$ mols. on long exposure to air, a little over 1 mol. at 100°, nearly the rest at 150°, but full dehydration of ajmaline takes place only at 200°, whereby it is partially isomerised. The same isomerised product, which it is proposed to call *iso*ajmaline, was also obtained on boiling ajmaline with caustic potash, though not sufficiently pure for analysis. In view of the respective mono and diacidic character of ajmaline and *iso*ajmaline, and considering the absence of any hydroxyl, methoxyl or methylene oxide groups in them, the two oxygen atoms in ajmaline could be provisionally accounted for as forming part of a labile betaine grouping and the formulae for ajmaline (I) (for which RNH·Me was suggested in the previous paper) and *iso*ajmaline (II) represented respectively as:

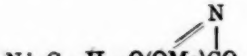


(I) (II)

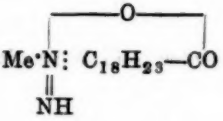
This would also largely explain the tenacity with which the last $\frac{1}{2}$ mol. of water sticks on to ajmaline, in so far as betaines are known to give up a part of their water of crystallisation with difficulty.

A revision of the formulæ of ajmalinine and serpentine through micro-analysis of the hydrated and the completely dehydrated bases show that while the C,H values reported in the first communication on the subject (*J. Indian Chem. Soc.*, 1931, **8**, 667) fully agree with those of the macro-analysis, the substance in the macro N estimation apparently could not be completely combusted, and that both the bases contain 2 nitrogen atoms like ajmaline, their formulæ working out to $C_{20}H_{26}O_3N_2$ (M.W., 342) and $C_{20}H_{20}O_3N_2$ (M.W. 336) respectively instead of $C_{20}H_{23}O_4N$ (M.W. 341) and $C_{21}H_{23}O_4N$ (M.W. 353). The original Cl and Pt values remain good for the hydrochlorides and the chloroplatinates of the bases for the altered formulæ inspite of the large reduction in the molecular weight of serpentine, the Cl found (*J. Indian Chem. Soc.*, 1931, **8**, 667) being theoretical for the original and 0·4% too low for the altered formula and Pt (*loc. cit.*) 0·4% too high for the original and 0·56% too low for the altered formula. The formula for serpentinine also has now been fixed through micro-analysis as $C_{20}H_{20}O_5N_2$.

Ajmalinine, as already reported, is tertiary, contains no N-Me but an OH (now also supported through the formation of a benzoyl derivative) and a methoxyl group. Its relation to ajmaline, keeping to the formula suggested for it above, could thus be tentatively indicated by the formulae:

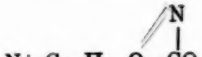


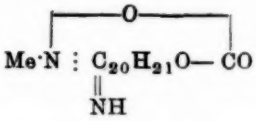
Ajmalinine.



Ajmaline.

corresponding in a measure to the structural difference between strychnine and methylstrychnine respectively:





On heating ajmalinine to 200° in an atmosphere of hydrogen it is partially degraded, the molten mass yielding back some ajmalinine and an optically inactive crystalline product answering to the formula $C_{13}H_{17}O_3N$ (m. p. 272° decomp.) and named as *apo*ajmalinine.

Serpentine which is tertiary in character and contains one OH and one OMe, differs from ajmalinine in containing 6 atoms hydrogen less in its molecule. In so far as its 3 oxygen atoms are already accounted for through hydroxyl, methoxyl and the suggested betaine grouping and it also fails to give qualitative tests for a quinone neucleus, its colour may be considered as originating from its higher grade of unsaturation. It was originally suggested (Part I, *loc. cit.*) that serpentine might be a secondary base like ajmaline as it gave a precipitate with nitrous acid, but on isolation and crystallisation it gave an analysis corresponding to a nitrous acid salt. Serpentine contains one olefine double bond like ajmaline, but of the two bromine atoms taken up by it in the cold, one appears to be secondarily eliminated as HBr, which adds on to the basic N, whereby a crystalline bromoserpentine hydrobromide is obtained. On heating serpentine to 210° in an atmosphere of hydrogen it is partially isomerised like ajmaline, yielding a crystalline substance melting at 256° and differing from it in yielding a stable gold salt.

Serpentinine appears to be a dioxidation product of serpentine, but it materially differs from it in being secondary in character as shown by its forming a nitroso derivative. Its active H contents could not be determined after Zerewitinoff owing to its sparing solubility in both amyl ether and pyridine but it definitely showed the presence of 1 OMe in its molecule and the absence of N-Me.

The red colouration given by nitric acid with the alkaloidal principle isolated from *Rauwolfia serpentina* by Warden and Bose (*Pharm. J.*, **23**, *iii*, 101; "Pharmacographia Indica," Vol. III, Append., 173-76) led them to suggest its relationship to the strychnos alkaloids by calling it '*pseudo* brucine.' This view found a further measure of support in van Itallie and Steenhauer's (*loc. cit.*) qualitative tests for ammonia, quinoline, carbazole and skatol in the zinc distillation product of their rauwolfine. It was partly on this basis that the Dutch authors supported their C_{21}-formula for rauwolfine suggesting its isomerism with tetrahydrostrychnine, $C_{21}H_{26}O_2N_2$. An important feature of variance with these suggestions is contained in the fact that the ajmaline series of alkaloids could not have more than 19 carbon atoms in their main structure as against 21 in the strychnine series. Considering, however, the formation of a monosulphonic acid, trinitro and dibromo derivatives of ajmaline and the probable presence of a betaine grouping in the whole series, it would not be surprising if the ring system of ajmaline should be similar in its main features to that of strychnine.

EXPERIMENTAL.

Ajamline ($C_{20}H_{26}O_2N_2$).

iso*Ajmaline* was obtained on repeated crystallisation of pyroajmaline (*loc. cit.*) from ethyl acetate. It melted at 265-66° and in 0·508% absolute alcoholic solution it showed $[\alpha]_D^{32} = +72·8°$ as against + 128° of ajmaline hydrate. [Found: (after dehydration at 150° in an atmosphere of hydrogen), C, 73·54; H, 7·86; N, 8·56; (after dehydration at 100° in *vacuo* over P_2O_5), C, 73·50; H, 8·0; N, 8·42; (after drying in air at room temperature), C, 73·7; H, 7·95; N, 8·46 $C_{20}H_{26}O_2N_2$ requires C, 73·6; H, 8·0; N, 8·6 per cent]. Determination of OMe in *iso*ajmaline after Zeisel gave a negative result, but 1 N-Me after Herzig and Meyer and 1 active H after Zerewitinoff were found to be present. (Found: Me, 4·0; H, 0·35; $C_{20}H_{26}O_2N_2$ requires for 1 N-Me and 1 active H, Me, 4·6; H, 0·30 per cent).

The *hydrochloride* in 0·4% solution in distilled water showed $[\alpha]_D^{32} = +98·7°$. (Found: Cl, 17·5. $C_{20}H_{26}O_2N_2$, HCl requires Cl, 17·5 per cent).

The *chloroplatinate*, prepared by adding aqueous platinic chloride to a solution of the *iso*-base in dilute hydrochloric acid under ice cooling, formed a dirty yellow mass, which quickly turns brown and melts at 227-28° (decomp.).

The iso-*picrate* was obtained as a bright yellow amorphous powder on adding an aqueous solution of picric acid to an aqueous solution of the *iso*-hydrochloride. It is soluble in warm water and alcohol and crystallises from the solvent in spindle shaped needles which shrink at 100°, soften at 150-60° and slowly char from 180° to 200°.

Dibromoajmaline.—0·1684 G. of ajmaline dissolved in 2 c.c. of dry chloroform solution and titrated against bromine in dry chloroform solution with ice cooling, took up 0·10 g. bromine (calculated for one double bond, 0·085 g.). The titration was followed by means of potassium iodide starch paper. On evaporating off the solvent at room temperature and crystallising the residue from absolute alcohol the brominated product was obtained in long prismatic rods, which turn brown at 216° and melt at 230° (decomp.). It is soluble in ethyl acetate and dilute hydrobromic acid but insoluble in water. (Found: Br, 33·17. $C_{20}H_{26}O_2N_2Br_2$ requires Br, 33·05 per cent).

Trinitroajmaline.—To 0·3 g. of ajmaline in a test tube immersed in ice mixture were added a few drops of well cooled concentrated nitric acid, when the whole mass turned deep red in colour. On dilution with

ice-cold water a yellow amorphous powder was obtained, which failed to crystallise out from any of the solvents and melted at 238-58° (decomp.). [Found: C, 52·7; H, 5·45; N, 12·10. $C_{20}H_{26}O_2N_2(NO_2)_3$ requires C, 52·06; H, 5·20; N, 12·15 per cent].

Ajmaline monosulphonic acid.—0·4 G. of ajmaline with 1 c.c. of conc. sulphuric acid (96%, *d* 1·84) was heated at 100° for 10 minutes, the reaction mixture was well cooled and diluted with cold water (7 c.c.) when the sulphonated product separated out in clusters of prismatic rods (0·39 g.). It softens at 310° and melts at 319-20° (decomp.). It gives a blood red colouration with concentrated nitric acid, is difficultly soluble in water and nearly insoluble in alcohol. (Found: C, 58·6; H, 6·53; N, 6·34; S, 7·8. $C_{20}H_{25}O_2N_2{\cdot}SO_3H$ requires C, 59·1; H, 6·4; N, 6·89; S, 7·88 per cent).

Ajmaline monoammonium sulphonate.—On passing gaseous ammonia into a suspension of ajmaline monosulphonic acid in alcohol a clear solution was obtained from which the ammonium salt precipitated out on addition of ether in prismatic rods and plates which shrink at 262°, melt at 319-20° (decomp.), and are difficultly soluble in water or alcohol.

Ajmaline barium sulphonate was obtained in clusters of prismatic needles (m. p. 322-24°, decomp.), when a concentrated aqueous solution of barium chloride was added to an aqueous solution of ajmaline monoammonium sulphonate. [Found: Ba, 13·7. $(C_{20}H_{24}O_2N_2SO_3)_2.Ba$ requires Ba, 14·50 per cent].

Calcium, sodium and potassium ajmaline sulphonates were also obtained in prismatic needles when concentrated aqueous solutions of the chlorides of the metals were added to the ammoniacal solution of ajmaline monoammonium sulphonate. Ajmaline potassium sulphonate melted at 304-10° but the calcium salt remained unmelted up to 370°.

Ajmalinine ($C_{20}H_{26}O_3N_2$).

Ajmalinine, $C_{20}H_{26}O_3N_2$.—Micro-analysis after dehydration at 140° in hydrogen atmosphere (Found: C, 70·0; 69·97; H, 7·46; 7·89; N, 7·83; 7·85. $C_{20}H_{26}O_3N_2$ requires C, 70·20; H, 7·60; N, 8·20 per cent.). Macro value (*J. Indian. Chem. Soc.*, 1931, **8**, 667) (after drying at 100°): C, 70·4; H, 7·1. Ajmalinine after dehydration at room temperature gave C, 64·49; H, 7·56; N, 7·21. $C_{20}H_{26}O_3N_2$, $1\frac{1}{2}$ H_2O requires C, 65·04; H, 7·86; N, 7·59 per cent. It showed an absence of N-Me after the method of Herzig and Meyer and presence of OMe after Zeisel. [Found: OMe, 8·80. $C_{20}H_{26}O_3N_2$

requires OMe (for 1 OMe) 9·06 per cent]. Its active H determination after complete dehydration at 140° in an atmosphere of hydrogen after Zerewitinoff in pyridine solution showed the presence of 1 active H. [Found: H, 0·35. $C_{20}H_{26}O_3N_2$ requires [illegible] (for 1 active H) 0·29 per cent].

Benzoylajmalinine was obtained through benzoyl chloride in pyridine solution as an amorphous powder which frothed up at 100° and melted at 140-50°. It was soluble in nearly all the organic solvents and failed to crystallise from any of them. (Found: C, 71·84; H, 6·60; N, 6·20. $C_{20}H_{25}O_3N_2{\cdot}CO{\cdot}C_6H_5$ requires C, 72·65; H, 6·73; N, 6·28 per cent.). Active H was found absent after Zerewitinoff. Its hydrochloride and picrate, prepared from the components in ethereal solution, formed amorphous powders both melting at 220° (decomp.). The chloroplatinate of the benzoyl base prepared from the hydrochloride melted at 242-45° (decomp.).

Ajmalinine methiodide.—To a solution (0·4 g., 1 mol.) of ajmalinine in chloroform (3 c.c.), methyl iodide (0·2 g., 1·2 mols.) was added and the mixture left well corked for one hour at room temperature, when ajmalinine methiodide separated as a pasty mass which crystallised from absolute alcohol in elongated rods, melting at 233-34° (decomp.). It is soluble in alcohol and water. It showed the presence of 1 N-Me after the method of Herzig and Meyer [Found: Me, 3·0. $C_{20}H_{26}O_3N_2{\cdot}CH_3I$ requires Me (for 1 NMe), 3·11 per cent. and 1 OMe after Zeisel. (Found: OMe_3, 6·7. $C_{20}H_{26}O_3N_2{\cdot}CH_3I$ requires OMe (for 1 OMe), 6·4 per cent].

Effect of heat on ajmalinine: apo*ajmalinine*.—On heating for 2 hours at 150° ajmalinine did not show any loss of weight but after 5 hours at 210° in hydrogen atmosphere it suffered a loss of 16·6%. The cream coloured substance, thereby obtained, could be separated into an ethyl acetate-soluble and an ethyl acetate-insoluble fraction. The former yielded back unaffected ajmalinine (m.p. 181-82°). On adding ethyl acetate to a solution of the ethyl acetate-insoluble fraction in methyl alcohol till turbidity, *apo*ajmalinine crystallised out in rectangular plates which were optically inactive and melted at 270-72°. After dehydration at 150° in an atmosphere of hydrogen it gave C, 65·6; H, 7·46; N, 6·11. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·20; N, 5·90 per cent. Its hydrochloride, prepared by adding the components in chloroform ether solution, melted at 243-44° (decomp.) and was soluble in alcohol and water. The picrate, obtained in a similar manner from the components, melted at 231-32°.

Serpentine ($C_{20}H_{20}O_3N_2$).

Serpentine.—Micro-analysis after dehydration at 150° in an atmosphere of hydrogen gave C, 71·16, 71·19; H, 5·69, 5·79; N, 8·06, 8·06. $C_{20}H_{20}O_3N_2$ requires C, 71·43; H, 5·95; N, 8·33 per cent. Micro-analysis after dehydration at room temperature (35°) gave C, 65·6; H, 6·28; N, 7·74 $C_{20}H_{20}O_3N_2$, $1\frac{1}{2}H_2O$ requires C, 66·10; H, 6·34; N, 7·71 per cent. The macro value after dehydration at 100° (*J. Indian Chem. Soc.*, 1931, 7, 667): C, 71·33; H, 6·3 per cent. Its active H determination in pyridine solution (after drying the base at 150° in hydrogen atmosphere) after the method of Zerewitinoff showed the presence of 1 active H. [Found: H, 0·26. $C_{20}H_{20}O_3N_2$ requires active H, (for 1 active H), 0·29 per cent]. It showed the absence of N-Me after the method of Herzig and Meyer.

Action of nitrous acid on serpentine: *serpentine nitrite*.—To a cooled solution of serpentine (1 mol., 0·34 g.) in 10% acetic acid a well cooled solution of sodium nitrite (1·5 mols., 0·1 g.) was slowly added and the reaction mixture was left for 4 hours at room temperature. The precipitate which separated was filtered and washed with a little water. It crystallised from absolute alcohol, alcohol-water, and alcohol-ether in cream coloured stars of needles which melted at 165-66° (decomp.). (Found: C, 62·38; H, 5·42; N, 10·30. $C_{20}H_{20}O_3N_2.HNO_2$ requires C, 62·67; H, 5·48; N, 11·0 per cent).

Serpentine methiodide.—To a solution of serpentine (1 mol.) in chloroform, methyl iodide (1·5 mols.) in chloroform was added with cooling, and the mixture left well corked at room temperature. The methiodide which slowly separated out was crystallised from alcohol-water, when it formed slender needles melting at 271-72° (decomp.). (Found: N, 5·28; I, 26·82. $C_{20}H_{20}O_3N_2$, CH_3I requires N, 5·86; I, 26·55 per cent). It showed 1 N-Me after Herzig and Meyer and 1 OMe after Zeisel [Found: Me 2·50; OMe 6·57. $C_{20}H_{20}O_3N_2.CH_3I$ requires Me (for 1 N-Me), 3·13; and OMe (for 1 OMe), 6·48 per cent].

Bromoserpentine hydrobromide.—0·2058 G. in 2 c.c. of dry chloroform titrated against bromine in the cold took up 0·11 g. of bromine (calculated for 1 double bond 0·098 g.). Owing to the reddish colour of the solution the titration was followed by means of potassium iodide starch paper. The residue left on evaporating off the solvent at room temperature crystallised from absolute alcohol in pale yellow

needles, which were soluble in water, insoluble in ethyl acetate or ether and melted at 257-58° (decomp.). (Found: Br, 31·48. $C_{20}H_{19}O_3N_2Br{\cdot}HBr$ requires Br, 32·26 per cent).

Effect of heat on serpentine: iso*serpentine*.—Serpentine is very difficultly dehydrated at 100° in *vacuo* over P_2O_5 and took 50 hours to reach a constant weight at that temperature losing 11·05%. The dehydrated base melted at 185-86° and became dark red in colour but when rubbed with alcohol or water the bright yellow colour of the hydrate and the melting point 158° were restored. On drying at 140° in an atmosphere of hydrogen there was no further appreciable loss in weight. On heating serpentine at 210° for about half an hour in hydrogen atmosphere a brown mass was produced from which *iso*serpentine was obtained which crystallised from absolute alcohol in prismatic rods melting at 230-32° (decomp.). It is very sparingly soluble in chloroform and ether and in contrast to serpentine easily soluble in alcohol. On dehydration in an atmosphere of hydrogen at 140° it lost 11·72% ($2\frac{1}{2}$ mols. require 12·5%). [Found: (after dehydration at 100° in *vacuo* over P_2O_5): C, 69·05; H, 5·76. $C_{20}H_{20}O_3N_2{\cdot}\frac{1}{2}H_2O$ requires C, 69·56, H, 6·09 per cent. (After dehydration at 140° in an atmosphere of hydrogen), N, 7·91. $C_{20}H_{20}O_3N_2$ requires N, 8·33 per cent].

The residue obtained on removal of the solvent from the mother liquors of *iso*serpentine formed a dark brown powder, which was easily soluble in chloroform and ethyl acetate, frothed up 120-22° and melted at 230-32° (decomp.). It thus appeared to be a mixture of affected serpentine and *iso*serpentine. (Found: C, 70·64; H, 6·0; N, 8·45. $C_{20}H_{20}O_3N_2$ requires C, 71·43; H, 5·95; N, 8·33 per cent).

The iso-*hydrochloride* was obtained on cooling the concentrated solution of the *iso*-base in alcoholic hydrochloric acid as spindle shaped needles. On drying in *vacuo* over P_2O_5 at 100° it lost 5·5% and melted at 271-72°. It was soluble in alcohol and water and insoluble in 10% hydrochloric acid. It showed a rotation in 0·488% aqueous solution $[\alpha]_D^{32} = +168{\cdot}08°$. (Found: Cl, 9·53. $C_{20}H_{20}O_3N_2{,}HCl$ requires Cl, 9·53 per cent).

The iso-*chloroplatinate* was prepared by adding a 10% aqueous solution of platinic chloride to an alcoholic solution of the hydrochloride of the base with cooling, when the chloroplatinate was obtained in slender needles which melted at 248-49° (decomp.). [Found: Pt, 18·10. $(C_{20}H_{20}O_3N_2{\cdot}HCl)_2{\cdot}PtCl_4$ requires Pt, 18·46 per cent].

The iso-*aurichloride* was prepared by adding an aqueous solution of gold chloride to a well cooled alcoholic solution of the *iso*-hydrochloride. The precipitate thereby formed was filtered, washed with water and alcohol and finally with ether and dried in *vacuo* over P_2O_5. The aurichloride, thus obtained, formed a buff coloured powder which softened at 174° and melted at 194-95° (reddening). [Found: Au, 29·00. $(C_{20}H_{20}O_3N_2 \cdot HCl)AuCl_3$ requires Au, 29·84 per cent].

The *picrate* was obtained by adding ethereal picric acid to a methyl alcoholic solution of the *iso*-base and crystallising the sticky precipitate from dilute alcohol when it formed crowded clusters of needles. It crystallised in elongated prisms from absolute alcohol. It is soluble in alcohol and insoluble in water, reddens at 250° and melts at 263-64° (decomp.).

Serpentinine ($C_{20}H_{20}O_5N_2$).

Serpentinine ($C_{20}H_{20}O_5N_2$).—It crystallises from dilute alcohol with $1\frac{1}{2}$ mols of water, of which it gives up $\frac{1}{2}$ mol. at 100° and the remaining 1 mol. at 150°. [Found (after dehydration at 150°): C, 64·84, 64·96; H, 5·76, 5·47; N, 7·19; 7·21. $C_{20}H_{20}O_5N_2$ requires C, 65·0; H, 5·44; N, 7·61 per cent. (After dehydration at 100° in *vacuo* over P_2O_5): C, 62·61; H, 5·77. $C_{20}H_{20}O_5N_2$, 1 H_2O requires C, 62·18; H, 5·70 per cent. (After drying at room temperature): C, 61·36; H, 5·80; N, 6·80. $C_{20}H_{20}O_5N_2$, $1\frac{1}{2}$ H_2O requires C, 60·67; H, 5·82; N, 7·09 per cent]. Its active H could not be determined owing to its sparing solubility in both amyl ether and pyridine; it showed the absence of N-Me and presence of 1 OMe. [Found: OMe, 7·90, 8·07. $C_{20}H_{20}O_5N_2$ requires OMe (for 1 OMe) 8·42 per cent]. Serpentinine hydrochloride, originally reported to be as an amorphous powder melting at 260-62°. could be crystallised from alcohol-ether in amber coloured spear-shaped rods, which melted at 271-72° (decomp.). (Found: Cl, 8·60. $C_{20}H_{20}O_5N_2$, HCl requires Cl, 8·78 per cent). and showed a rotation in 0·26% aqueous solution $[\alpha]_D^{32} = +166\ 93°$. The *picrate* reported earlier as melting at 225-27°, crystallised from concentrated solutions of alcohol in silky prismatic rods and from methyl alcohol-ether in spear shaped rods melting at 263-64° (decomp.). The chloroplatinate prepared from the hydrochloride as already reported gave Pt, 17·70. $(C_{20}H_{20}O_5N_2, HCl)_2PtCl_4$ requires Pt, 17·04 per cent.

The *aurichloride* was obtained by adding 1% aqueous solution of gold chloride to a well cooled aqueous solution of the hydrochloride.

It forms a yellowish brown amorphous powder which is insoluble in water and melts at 194-95° (decomp.). [Found (in air-dried gold salt): Au, 27·5. ($C_{20}H_{20}O_5N_2$, HCl). $AuCl_3$ requires Au, 27·85 per cent].

The *hydrobromide* was obtained as a paste on treating the base with dilute hydrobromic acid, which crystallised from its solution in hot water in stars of needles melting at 271-72° (decomp.). It is difficultly soluble in cold water and alcohol.

The *hydroiodide* was obtained by adding a concentrated solution of potassium iodide to an aqueous solution of the hydrochloride as an amber coloured powder sparingly soluble in warm water and alcohol, m.p. 271-72° (decomp.).

Action of nitrous acid on serpentinine: nitrososerpentinine.—To a cooled solution of serpentinine (1 mol. 0·37 g.) in 10 c.c. acetic acid, a well cooled solution of sodium nitrite (1·5 mols. 0·1 g.) was slowly added with shaking when a cream yellow crystalline product separated out. After keeping the reaction mixture overnight at room temperature the precipitate was well washed with dilute acetic acid and then with water to remove any unreacted base and crystallised from dilute alcohol, when a hydrate of nitrososerpentinine was obtained in brooms of broad needles melting at 159-60°. Dried in *vacuo* at 100° over P_2O_5 it lost 5·67; $1\frac{1}{2}$ H_2O requires 6·4 per cent. [Found (after dehydration): C, 59·90; H, 5·44. $C_{20}H_{20}O_5N_2 \cdot NO$ requires C, 60·45; H, 4·78 per cent. (Air-dried nitroso serpentinine): N, 9·6. $C_{20}H_{20}O_5N_2 \cdot NO$, $1\frac{1}{2}$ H_2O requires N, 9·95 per cent].

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A Note on the Influence of Acidity of Agar on the Liesegang Rings of Lead Chromate and Lead Iodide.

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It is well known that good rings of lead chromate are obtained in some samples of agar, while in others they are not observed at all. With traces of acetic acid, the rings are somewhat well defined and slightly further apart (Hatscheck, *Proc. Roy. Soc.*, 1921, **A 99**, 496). Results on the influence of the degree of acidity of agar on the Liesegang rings of lead chromate and lead iodide are given in this paper (*cf.* Desai and Nabar, *J. Indian Chem. Soc.*, 1932, **9**, 141; Desai and Naik, *ibid.*, 1934, **11**, 59).

Experimental.

Rings of lead chromate in agar.—Chemically pure agar powder (3·9 g.) soaked in distilled water (200 c.c.) for 24 hours was heated on a water-bath for nearly 1½ hours, and loss of water during heating being made good by addition of fresh, distilled water. In thoroughly cleaned and dried test tubes of the same internal diameter, 12 c.c. of agar, 4·0 c.c. of a 0·5% lead acetate and suitable amounts of acetic acid or sodium acetate were added. The p_H of the agar solution thus varied from 2·4 to 9·25, p_H of original agar being 5·94 (colorimetric). The total volume was made the same (20 c.c.) with distilled water, the contents of each test tube were stirred and allowed to stand for 24 hours to set to a gel. 3 C.c. of a 1% solution of potassium chromate were allowed to diffuse at the top of the gel in each test tube. The changes in the test tubes were frequently noted each day until potassium chromate had diffused right upto the bottom of the test tube. Only normal bands were obtained, the anomalous bands (Hatscheck, *loc. cit.*) being absent due to the test tubes having not been exposed to light. The distances between successive rings were measured by

means of a cathetometer. The following is the summary of observations:

(*i*) No well defined rings were obtained in samples of agar having a p_H range from 2·4 to 2·96, as well as those having p_H higher than about 9·25. Samples of agar of p_H 3·08 to 9·02 gave well defined rings.

(*ii*) The time for the appearance of the first ring increases with an increase of the p_H of the gel.

(*iii*) The distance between the successive rings increases with all samples of agar.

(*iv*) The thickness of the ring in any one sample of the gel increases from the first ring to the last ring, but its compactness decreases at the same time.

(*v*) The distance between successive rings decreases with an increase of p_H, the number of rings increasing at the same time.

(*vi*) The thickness of the rings decreases with an increase of p_H of agar.

(*vii*) The size of particles in the rings increases with an increase of p_H upto 8·04, the particles being again smaller in samples of gel having p_H higher than this value.

Rings of lead iodide in agar.—The details of the experiments were exactly the same as in the case of rings of lead chromate except that in this case, the gel was impregnated with 2 c.c. of a 40% solution of potassium iodide and 3·0 c.c. of a 30% solution of lead nitrate were added at the top for diffusion after setting of the gel. The total volume in this case was also made to 20 c.c. by adding suitable amounts of distilled water. The following is the summary of the results:

(*i*) The time for the appearance of the first ring generally increases with an increase of the p_H of the gel.

(*ii*) Good well-defined rings are obtained in samples of agar having a p_H range from 2·40 to 5·94; broken rings are obtained in samples of gel of p_H higher than 6.

(*iii*) The distance between successive rings in any sample of gel increases from the first ring to the last ring, but its compactness decreases at the same time.

(*iv*) The distance between the successive rings decreases with an increase of p_H, the number of rings increasing at the same time upto p_H value of about 8.

(*v*) The thickness of rings decreases with an increase of p_H of agar.

(*vi*) The size of particles in the rings increases with an increase of p_H of the sample of the gel.

The results show that there is a definite range of p_H of the agar gel within which good rings of lead chromate and lead iodide can be obtained.

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Hydrazinates of Metallic Thiosulphates.

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Several investigators (Curtius and Schrader, *J. pr. Chem.*, 1894, *ii*, **50**, 311 ; Hofmann and Marburg, *Ber.*, 1897, **30**, 2019 ; Franzen and Mayer, *Z. anorg. Chem.*, 1909, **50**, 247 ; Franzen and Lueking, *ibid.*, 1911, **70**, 145) have shown that hydrazine combines with many metallic salts, especially with those of the transitional elements, to form complex compounds similar to those given by ammonia and ethylenediamine. This tendency to complex-formation with hydrazine is pronounced even in the case of unstable and insoluble salts, as illustrated by the formation of hydrazinates of sulphites and nitrites of Mn, Co, Ni, Zn, and Cd (Rây and Goswami, *Z. anorg. Chem.*, 1928, **168**, 329) and of the corresponding thiocyanates (Rây and Sarkar, *J. Chem. Soc.*, 1920, **117**, 321). In all these cases the prominent type is tetra-co-ordinated, with one or two exceptions, assuming that the hydrazine molecule acts as a bidentate group like ethylenediamine, e.g. $—NH_2—NH_2—$. With nickel sulphite only, it exhibits a co-ordination number of six, with cadmium sulphite it falls down to two, with cobalt nitrite it is three (*cf.* Rây and Goswami, *loc. cit.*).

In the case of salts with anions of stronger acids, formation of both hexa- and tetra-co-ordination has been observed, and it is generally assumed that the highest or limit co-ordination number is more frequently exhibited by the metals in their salts with stronger acids,

In the present paper hydrazinates of metallic thiosulphates, which have not yet been described in the literature, have been studied. Hexa-co-ordinated compounds of the composition, $[M(N_2H_4)_3]\ S_2O_3$, have been prepared, where M = Co, Ni, Zn, or Cd ; nickel gives also a tetra-co-ordinated salt. Attempts to prepare complexes of 4-co-ordination type with Co, Zn and Cd have met with no success. This furnishes an additional proof of the influence of the anion on the co-ordination number of the central metallic atom. The tendency of S_2O_3'', an anion of a fairly weak acid, to develop the maximum co-ordinating capacity of the metallic atom, contrary to general assumption, is an instance in support of this specific anionic influence.

These hydrazinates are all insoluble, or very sparingly soluble, in water, and are easily decomposed by acids with evolution of SO_2 and precipitation of sulphur. With boiling water they are more or less slowly hydrolysed with formation of metallic hydroxides.

Experimental.

Trihydrazine-cobalt thiosulphate.—Cobalt acetate (1 g.), $Na_2S_2O_3$, $5H_2O$ (3 g.) and ammonium acetate (2·5 g.) were dissolved in the least quantity of cold water. The solution was filtered, cooled in ice, and then added, drop by drop, to an excess of a concentrated solution of hydrazine hydrate. The light yellow granular precipitate was filtered, washed at first with ice-cold water and then with alcohol. The substance was dried in *vacuo* over H_2SO_4. {Found: N, 31·3, 31·48 ; S, 24·0, 23·97, 24·0 ; Co, 22·0, 22·1, 22·32. $[Co(N_2H_4)_3]S_2O_3$ requires N, 31·46 ; S, 23·90 ; Co, 22·08 per cent}.

The compound, when heated in a dry test tube, gives out hydrazine with formation of CoS. The dry salt, on keeping for a long time in air, slowly decomposes forming CoS.

When a dilute solution of hydrazine hydrate was added to a mixture of an excess of cobalt acetate, sodium thiosulphate and ammonium acetate solution, dihydrazinate was precipitated in the form of a dirty cream coloured powder, but it readily decomposed on the filter with formation of cobalt hydroxides.

Trihydrazine-nickel thiosulphate.—Nickel acetate (1 g.), sodium thiosulphate (3 g.) and ammonium acetate (2·5 g.) were dissolved in the least quantity of water. The solution was filtered, cooled in ice and then added, drop by drop, to an excess of cooled, concentrated solution of hydrazine hydrate with constant stirring. The granular pink precipitate was washed and dried as in the previous case.

{Found : N, 30·45, 30·90 ; S, 23·0, 22·80; Ni, 21·27, 21·30. $[Ni(N_2H_4)_3]\,S_2O_3.\,\frac{1}{2}\,H_2O$ requires N, 30·46 ; S, 23·20; Ni, 21·28 per cent}. The properties resemble those of the corresponding cobalt compound.

Dihydrazine-nickel thiosulphate.—To a cold solution, containing nickel thiosulphate (1 g.) and ammonium thiosulphate (2·5 g.), a well cooled dilute solution of hydrazine hydrate was added, drop by drop, with constant stirring, when a light blue granular precipitate was produced. This was washed and dried as before. {Found : N, 21·10, 21·40; S, 24·0, 24·43; Ni, 22·60, 22·45. $[Ni\,(N_2H_4)_2]\,S_2O_3,\,1\frac{1}{2}H_2O$ requires N, 21·39; S, 24·45; Ni, 22·40 per cent}. Its properties are similar to those of the trihydrazinate.

Trihydrazine-zinc thiosulphate.—Zinc acetate (1 g.), sodium thiosulphate (3 g.) and ammonium acetate (2·5 g.) were dissolved in the least quantity of water. The solution, cooled in ice, was then added dropwise to an excess of concentrated hydrazine hydrate solution. The white crystalline precipitate formed was kept in ice-water for an hour or two, then filtered, and washed at first with water containing some hydrazine and finally with alcohol. This was then dried as before. {Found : N, ..., 30·77; S, 23·50, 23·60 ; Zn, 23·70, 24·0. $[Zn(N_2H_4)_3]S_2O_3$ requires N, 30·70; S, 23·40; Zn, 23·90 per cent}.

Trihydrazine-cadmium thiosulphate.—Cadmium acetate (1 g.) and sodium thiosulphate (3 g.) were dissolved in the least quantity of cold water, the ice-cooled solution was then added dropwise to an excess of ice-cold concentrated hydrazine hydrate solution. The white crystalline precipitate formed was washed and dried as in the case of zinc compound. {Found : N, 26·20; S, 19·70 ; Cd, 35·15. $[Cd(N_2H_4)_3]S_2O_3$ requires N, 26·20 ; S, 19·90; Cd, 35·08 per cent}.

On keeping in air, the substance slowly decomposes with formation of yellow cadmium sulphide.

Method of analysis.—Cobalt and cadmium were estimated as sulphates after decomposition of the substance with sulphuric acid. Sulphur was estimated as sulphate after oxidation of the compounds with ammoniacal hydrogen peroxide. Hydrazine was estimated as nitrogen gas by oxidation with alkaline ferricyanide (*cf.* Rây and Sen, *Z. anorg. Chem.*, 1912, **76**, 380). Nickel and zinc were estimated as nickel dimethylglyoxime and zinc ammonium phosphate respectively after decomposing the compounds with Br_2-water.

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On the Synthesis of Higher Paraffins from Water Gas. The use of Promoters for Activating Iron-copper Catalyst.

By J. C. Ghosh and Sukumar Sen.

"In April, 1926, Fischer and Tropsch (*Brennstoff-Chemie*, 1926, 7, 97 ; *Ber.*, 1926, **59B**, 830, 832) announced that higher homologues of methane up to solid paraffin together with inappreciable quantities of olefines were formed when water gas was passed at atmospheric pressure over catalysts of iron and cobalt around 270°. Elvins and Nash (*Fuel*, 1926, **5**, 263) confirmed this and in July (*Nature*, 1926, **118**, 154), reported the presence of oxygen-containing compounds in a product obtained on a cobalt catalyst. Closer examination of the oil by Elvins (*J. Soc. Chem. Ind.*, 1927, **46**, 473T) further confirmed this. In September, 1927, Smith, Davis, and Reynolds gave preliminary results in which olefines as well as paraffins were obtained; complete results were published in 1928 (*Ind. Eng. Chem.*, 1928, **20**, 462). In 1928, Fischer and Tropsch (*Brennstoff-Chemie*, 1928, **9**, 21) gave results of exhaustive examination of hydrocarbons obtained by them and stated that O_2-containing compounds were present only in small quantities (traces of benzene and toluene were also obtained) besides olefines and paraffins.

Fischer supposed the mechanism to centre round carbide formation. Elvins and Nash suggest that the formation of O_2-containing compounds is an intermediate step in the formation of hydrocarbons. Elvins suggests that carbonyls are the intermediate products. The latest ideas of Fischer and Tropsch as to the possible mechanism of the process are: (*i*) CH_2 may be primarily formed from H_2 and carbide carbon followed by polymerisation, (*ii*) complex molecules of 3 or 4C atoms may form as a primary act and may undergo (*a*) polymerisation or (*b*) cracking on the catalyst, (*iii*) secondary hydrogenation always occurs (Smith and co-workers, *J. Amer. Chem. Soc*, 1930, **52**, 3221)."

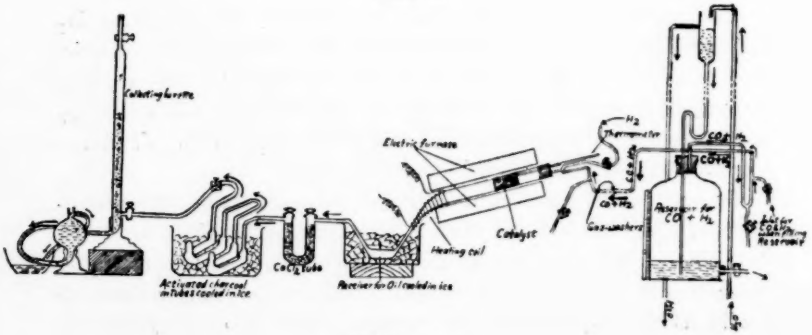
In support of mechanism (*iii*), Fischer and Pichler (*Brennstoff-Chemie*, 1929 **10**, 279) and Fischer, Peters and Coch (*ibid.*, 1929, **10**, 383) showed that acetylene could of itself or in presence of H_2 or water gas, be converted into liquid hydrocarbons under suitable conditions of experiment; for example, with 10% acetylene in

water gas, Fe-Cu or Fe-Ni catalysts were found suitable. Smith and co-workers (*loc. cit.*) however found that with a Fe-Cu catalyst ethylene did not enter into any reaction with water gas, whereas Co-Cu-MnO_2 catalysts were satisfactory.

If CH_2 is the primary product which yields higher hydrocarbons by polymerisation, then any catalyst which helps the production of ethylene, the simplest polymer of $-CH_2-$ from water gas would increase the yield of hydrocarbons. A pure iron-copper catalyst does not help this reaction. It was accordingly felt that promoters might be found which would accelerate this interaction of ethylene even on a Fe-Cu catalyst base, and this investigation was undertaken principally with that end in view. Berl (*Z. angew. Chem.*, 1930, **43**, 435) has observed that the use of ZnO or MnO in a Fe-Cu catalyst, distinctly improves the yield of higher hydrocarbons. In this laboratory considerable work has been done on the promoter action of Ce and Th on nickel catalysts (Ghosh and Chakravarty, *J. Indian Chem. Soc.*, 1925, **2**, 150, 157; Ghosh, Chakravarty, and Bakshi, *Z. Elektrochem.*, 1931, **37**, 775; *Z. anorg. Chem.*, 1934, **217**, 277). In the present paper results obtained with Ni alone or Ni, Ce, and Th in the ratio 8·03 : 0·13 : 0·95 as promoters on Fe-Cu catalyst have been described.

Fischer's investigation of the high pressure conversion of water gas into synthol demonstrated that in the effluent gases the concentrations of the various gases did not remain constant but showed periodic variations with the progress of reaction. It was accordingly decided to determine quantitatively the composition of samples of gas mixture leaving the catalyst surface at intervals.

FIG. 1.



(Not to scale)

Experimental.

The experimental arrangement will be apparent from Fig. 1. A known volume of an approximately 1:1 mixture of CO (from formic acid) and H_2 was prepared in the aspirator bottle. The gas was passed through washers containing the usual purifying agents to the reaction tube in the electric furnace at the desired temperature. The catalyst was held in the reaction tube between asbestos plugs and the bulb of the thermometer was embedded in the catalyst. The furnace was set in an inclined position to facilitate the removal of the solid and liquid products formed. The exit end of the tube was tapered downwards to a modified **U**-shaped receiver, which was kept immersed in ice during the progress of the experiment for the condensation of the more easily condensible portion of the product—the "heavy liquid hydrocarbons." The water formed was then removed by a $CaCl_2$ **U**-tube and the "light liquid hydrocarbons" removed by adsorption by means of active charcoal. Two charcoal tubes were used in series to ensure complete removal of the higher hydrocarbons. The exit end of the reaction tube up to a few inches inside the furnace, was kept heated by means of a heating coil in order to bring down the high melting products formed. For estimation the whole system was flushed with H_2 after the experiment was over and the receiver was cut off just above the point where the solids collected, weighed, and connected with two **U**-tubes containing dehydrite, one at each end, to remove the water mixed with the hydrocarbons. The weights of the receiver after removal of water and after it had been cleaned and dried, gave the weights of the heavy hydrocarbons and the water condensed with them.

The estimation of the light liquid hydrocarbons was effected by weighing before and after experiment, in each case after flushing with pure dry H_2 to constant weight. When flushing with H_2 after experiment, the charcoal tubes were kept immersed in an ice-bath to prevent any loss of adsorbed hydrocarbons. The exit gases were analysed by the usual gas analytical methods (the unsaturated hydrocarbons being determined by absorption with bromine water and the saturated hydrocarbons by explosion with oxygen) and the amount of contraction taking place determined at frequent intervals.

Preparation of catalysts.—The catalysts were prepared by the slow ignition of the nitrates on asbestos at the lowest temperature possible, soaked with $\frac{1}{2}\%$ solution of K_2CO_3, and dried. The catalyst base for

the promoter was always of the composition Fe: Cu=4:1 on 2·5 g. of asbestos impregnated with K_2CO_3. The catalysts were reduced in a slow current of H_2. For catalyst No. I the reduction was carried out at 330° for 12 hours. In the case of the other catalysts, the first stage of reduction was carried out at the lowest temperature at which water began to be produced rapidly, the second stage at the higher temperature at which water again appeared, and finally the temperature was raised to the desired point and reduction carried to completion.

General characteristics of the catalysts.—Graphical representation of the composition of the effluent gases always showed a periodic variation in the case of hydrogen and carbon dioxide gas, their maxima and minima practically occurring at the same time (*cf.* Fig. 2).

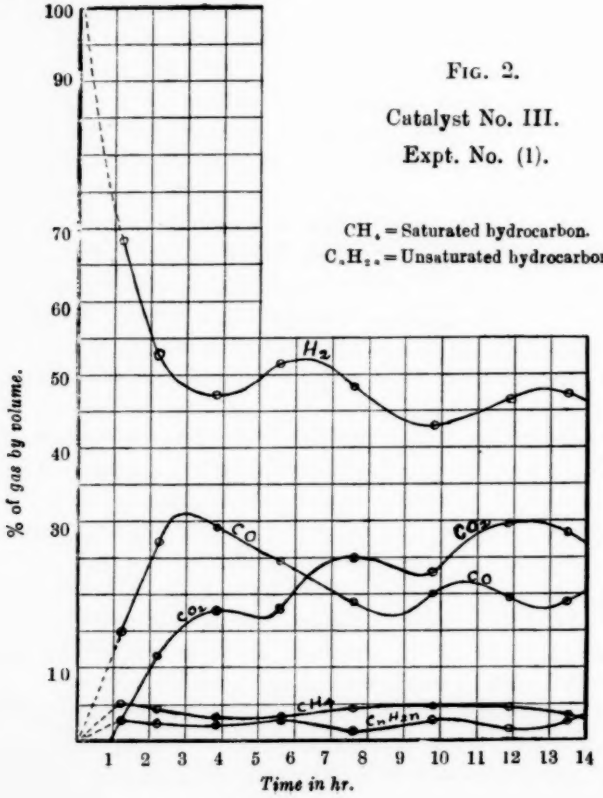


FIG. 2.

Catalyst No. III.

Expt. No. (1).

CH_4 = Saturated hydrocarbon.
C_nH_{2n} = Unsaturated hydrocarbon.

Rapid diminution in the concentration of CO in the effluent gases is also always associated with a regular increase in the concentration of CO_2. These results, therefore, indicate that the velocities of the following reactions on the catalyst suffer periodic variation:—

$$2CO = CO_2 + C \quad \ldots \quad \ldots \quad \ldots \quad (i)$$

$$C + H_2 = CH_2 \quad \ldots \quad \ldots \quad \ldots \quad (ii)$$

when the velocity of (*i*) is greater relative to (*ii*), concentrations of of CO_2 and H_2 in the effluent gases increase, and when after sufficient accumulation of active carbon on the catalyst surface, the velocity of (*ii*) relative to (*i*) increases, the concentrations of both CO_2 and H_2 diminish. Again, the concentration of H_2 in the first 2 hours is much larger than its average concentration during the next 12 hours, while the concentration of CO suffers an opposite change. As will be explained later, CO displaces the H_2 adsorbed on the surface of the catalyst during the process of formation of the hydrocarbons at the initial stages.

Products.—The heavy liquids melted within a range of 8° to 31°. The highest melting point of the solids was 81°.

Calculations.—The saturated hydrocarbons have been estimated as CH_4. Following approximate values of heat of combustion have been used in making the calculations (Landolt's Tables, 1923, p. 1588).

Unsaturated hydrocarbons	—	11800 cal. per g.
Saturated ,,	—	13340
Light liquid ,,	—	11360
Heavy liquid ,,	—	11300
Solid ,,	—	11200

Catalyst I.

Composition of the catalyst: Fe, 4 g. ; Cu, 1 g. ; Ni, 0·055 g.

Reduced at 330° for 12 hours.

Expt. (1).—The activity of the catalyst did not remain steady. The amount of CO in the effluent gases continued to increase and that of CO_2 to diminish. The yield of hydrocarbons was 8·1% by weight of the reacting gases at space velocity 63, 38·8% of the hydrocarbons formed being gaseous.

Expt. (2).—The catalyst was regenerated by heating in a current of H_2 for 3 hours at 330°. The regeneration was not effective. The percentage of CO was quite large from the beginning and continued to increase with the progress of the reaction; the amount of CO_2 continued to diminish simultaneously. The yield was 8·2% of the reacting gases by weight at space velocity 65, 41·7% of the hydrocarbons obtained being gaseous.

Expt. (3).—An attempt was made to regenerate the catalyst by prolonged heating in H_2. The hydrocarbons formed at one passage was 8·8% of the weight of the reacting gases but 76·4% of the total yield was gaseous. The space velocity was 65.

In Table I, experimental data for catalyst I in experiment (2) are recorded. Experiments (1) and (3) were carried out in a similar fashion, but the data being similar are not recorded here.

TABLE I.

Reaction temp. = 265°. Expt. period = 14 hr. 19 min. Rate of flow per min. = 10·8 c.c. Space velocity = 65.

	Composition of inflowing gas.			Residue.			Converted.		
	CO.	H_2.	Total.	CO.	H_2.	Total.	CO.	H_2.	Total.
Vol. (c.c.) ...	4700	4600	9300	2200	3280	5480	2500	1320	3820
Wt. (g.) ...	5·88	0·41	6·29	2·75	0·29	3·04	3·13	0·12	3·25
Heat of combustion (cal.)	14290	13910	28200	6680	9840	16520	7610	4070	11680

Products of reaction.

	CO_2.	Hydrocarbons. Gaseous.		Liquid.		Solid.	Water.	Total.	Total hydrocarbon.
		Unsatd.	Satd.	Heavy.	Light.				
Vol. (c.c.) ...	1101	90	130	...	...	...	...	1330	...
Wt. (g.) ...	2·18	0·17	0·12	0·13	0·07	0·07	0·24	2·98	0·56
Heat of combustion (cal.)	...	2010	1600	1470	800	780	...	6660	...

TABLE I (*contd.*).

To be accounted for.			Obtained.					
C.	O_2.	H_2.	C.		O_2.		H_2.	
1·34g.	1·79g.	0·12g.	From CO_2,	0·60 g.	From H_2O,	0·21 g.	From H_2O,	0·03 g.
			From hydrocarbons,	0·47 g.	From CO_2,	1·58 g.	From hydrocarbons,	0·09 g.
			Total	1·07 g.	Total	1·79 g.	Total	0·12 g.

Unaccounted for.		Remarks.
C	0·27 g.	Probably deposited on the surface of the catalyst.
O_2		
H_2		

Catalyst II.

Composition of the catalyst: Fe, 4 g.; Cu, 1 g.; Ni, 0·11 g.

Expt. (1).—Reduction of the catalyst by H_2 at 330° gave a sample whose catalytic activity did not remain steady as in the case of catalyst I. When the temperature of reduction was not allowed to exceed 300°, a considerable improvement in steadiness was noted. CO did not show a progressive increase but showed a marked periodic variation as also did H_2. The yield of hydrocarbons was 9·7% by weight at space velocity 64, the gaseous hydrocarbons being 36·2%.

Expt. (2).—The catalyst was regenerated by heating for 3 hours in H_2. The yield in this case was much better, *viz.*, 13%, at space velocity 64, the gaseous hydrocarbons being 46·2%.

Expt. (3).—The catalyst was heated for 3 hours at 300° before experiment. The yield of hydrocarbons was 12·1% by weight of the reacting gases at space velocity 56, the gaseous hydrocarbons being 33%.

In Table II, experimental data for experiment (2) with catalyst II are recorded.

TABLE II.

Reaction temp. = 265°. Expt. period = 13 hr. 23 min. Rate of flow = 10·6 c.c./min. Space velocity = 64.

	Composition of inflowing gas.			Residue.			Converted.		
	CO.	H_2.	Total.	CO.	H_2.	Total.	CO.	H_2.	Total.
Vol. (c.c.) ...	4250	4250	8500	1300	3070	4370	2950	1180	4130
Wt. (g.) ...	5·31	0·38	5·69	1·63	0·27	1·90	3·69	0·11	3·80
Heat of combustion (cal.). ...	12900	12890	25790	3960	9160	13120	8970	3730	12700

TABLE II (*contd.*).

	Products of reaction							
		Hydrocarbons						
	CO_2.	Gaseous		Liquid.		Solid.	Water.	Total.	Total hydrocarbon.
		Unsatd.	Satd.	Heavy.	Light.				
Vol. (c.c.)	1040	90	260	...	...	...	...	1390	...
Wt. (g.)	2·04	0·17	0·19	0·10	0·26	0·02	0·17	2·95	0·74
Heat of combustion (cal.)	...	2010	2540	1130	2950	220	...	8850	...

To be accounted for			Obtained.		
C.	O_2.	H_2.	C.	O_2.	H_2.
1·58 g.	2·11 g.	0·11 g.	From CO_2, 0·56 g. From hydrocarbons, 0·61 g.	From H_2O, 0·15 g. From CO_2, 1·48 g.	From H_2O, 0·02 g. From hydrocarbons 0·13 g.
			Total 1·17 g.	Total 1·63 g.	Total 0·15 g.

Unaccounted for		Remarks.
C, 0·41 g.	670 c.c. CO.	Hydrogen was used for flushing after expt. (1) and also for regenerating the catalyst. Excess of H_2 must be due to liberation of adsorbed H_2 and deficit in CO must be likewise due to adsorption on solid catalyst surface.
O_2, 0·48 g.		
H_2, 0·04 g. in excess.	450 c.c. H_2 in excess used up during reaction.	

Catalyst III.

The Ni content was 0·25 g. and in addition it contained 0·0041 g. of Ce and 0·0296 g. of Th. Reduction temperature, 260°.

Expt. (1).—The temperature of reaction was 238°. The experiment was continued for 14 hours. Conversion into hydrocarbons at one passage was 12·7% by weight of reacting gases, gaseous hydrocarbons being 49·4%, at space velocity, 64.

Expt. (2).—After the first experiment the whole system was flushed with H_2 at the reaction temperature of 230° for 2 hours. The result obtained was better than in the first experiment, 15·4% by weight of the reacting gas having been converted into hydrocarbons ; gaseous

hydrocarbons however formed 68·5 % of the total amount of hydrocarbons obtained; water formed was negligible, space velocity being 60.

Expt. (3).—For this experiment the catalyst was further reduced at 271°. The yield of hydrocarbons was 19·2% of the reacting gases by weight at space velocity 59, gaseous hydrocarbons being only 34·3 %.

In Table III experimental data with catalyst III for expt. (3) are recorded.

TABLE III.

Reaction temp.=256°. Expt. period=14 hrs. 6 min. Rate of flow=9·8 c.c./min. Space velocity=59.

	Composition of inflowing gas.			Residue.			Converted.		
	CO.	H_2.	Total.	CO.	H_2.	Total.	CO.	H_2.	Total.
Vol. (c.c.) ...	4070	4260	8330	660	2550	3210	3410	1710	5100
Wt.t. (g.) ...	5·09	0·38	5·47	0·83	0·23	1·06	4·26	0·15	4·41
Heat of combustion (cal.) ...	12370	12890	25260	2020	7800	9820	10350	5090	15440

Products of reaction.

	CO_2.	Hydrocarbons. Gaseous		Liquid.		Solid.	Water.	Total.	Total hydrocarbon.
		Unsatd.	Satd.	Heavy.	Light.				
Vol. (c.c.) ...	1440	100	220	...	...	...	...	1760	
Wt. (g.) ...	2·82	0·19	0·16	0·16	0·42	0·11	0·14	4·00	1·04
Heat of combustion (cal.)	...	2240	2140	1810	4770	1280	...	12190	

To be accounted for.			Obtained.		
C.	O_2.	H_2.	C.	O_2.	H_2.
1·83 g.	2·43 g.	0·15 g.	From CO_2, 0·77g.	From H_2O, 0·12g.	From H_2O, 0·02g.
			From hydrocarbons, 0·87 g.	From CO_2, 2·05g.	From hydrocarbons, 0·17g.
			Total 1·64g.	Total 2·17g.	Total 0·19g.

TABLE III (*contd.*).

Unaccounted for.		Remarks.
C, 0·19 g.		
O_2, 0·26 g.	340 c.c CO	Excess of H_2 and deficit in CO should be accounted for in the same way as in Table II.
H_2, 0·04 g. in excess	450 c.c. H_2	

While this investigation was in progress, Fischer and Koch (*Brennstoff-Chemie*, 1932 **13**, 61) published results obtained with the following catalysts:—Co + 18% Th or Co + 15% Mn, precipitated with alkaline carbonate. By continuous circulation of gases, the yield of liquid hydrocarbons approached 71% of the theoretical. In our experimental data recorded in Table III it will be seen that a single passage of water-gas above our catalyst at a space velocity of 59 gave 43·3% of the theoretical yield calculated on the basis of the equation,

$$3CO + 3H_2 = CO_2 + 2(CH_2) + H_2O.$$

This catalyst therefore appears to be very efficient one.

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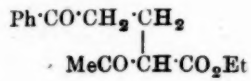
Addition of Compounds Containing Reactive Methylene Group with Phenylvinylketone.

BY S. M. ABDULLAH.

In a work to be published later on, large quantities of phenylvinylketone were obtained as a bye-product. Since it combines very readily with substances containing reactive methylene group, it can be used for making saturated ketonic compounds which are unsaturated in the β-position and which it is difficult to prepare in any other manner. Allen and Bridgess (*J. Amer. Chem. Soc.*, 1929, **51**, 2151) and Kohler (*Amer. Chem. J.*, 1909, **42**, 375) have also done some work in this line. The additive properties of this $\alpha\beta$-unsaturated ketone with substances containing reactive methylene group, *e.g.*

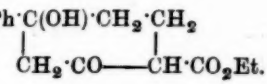
(*i*) acetoacetic ester, (*ii*) desoxybenzoin, (*iii*) phenylacetone and (*iv*) dibenzylketone have been studied in this paper. All these substances added themselves at the double bond of phenylvinylketone; in some cases, however, secondary reactions take place with the elimination of a molecule of water.

Acetoacetic ester gave with phenylvinylketone in the presence of sodium ethoxide an additive product (I or I*a*), but it very easily eliminated one molecule of water producing an unsaturated cyclic ketonic acid ester (II), which on saponification resulted in the unsaturated ketone (III). On treating with ozone in chloroform, (III) gave an ozonide which decomposed with water to benzoic and succinic acids.

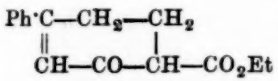


(I)

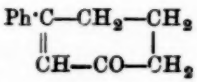
or



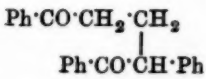
(I*a*)



(II)



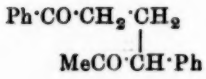
(III)



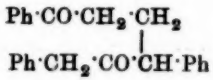
(IV)

Desoxybenzoin reacted with phenylvinylketone in the presence of sodium ethoxide forming a 1 : 5-diketone (IV).

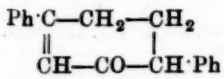
Benzylmethylketone and dibenzylketone gave instead of the expected addition products (V) and (VI), the unsaturated cyclic ketones (VII) and (VIII).



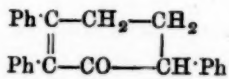
(V)



(VI)



(VII)



(VIII)

Experimental.

Addition of acetoacetic ester with phenylvinylketone.—(*a*). An equimolecular mixture of acetoacetic ester and phenylvinylketone (each 9 g.), kept cold by ice, was treated with sodium ethylate (1%, 10 c.c.). After one hour the solution was acidified with hydrochloric acid, extracted with ether, the ether removed and the residue distilled in vacuum at 12 mm., when the following fractions were obtained:—

(*i*) till 100° (7 g.), chiefly unreacted raw material.

(*ii*) 200-205° (8 g.), phenyl*cyclo*hexenonecarboxylic acid ester.

(*iii*) 300° (1 g.), chiefly polymerised phenylvinylketone.

(*b*). To an equimolecular mixture of dimethylaminopropiophenone (18 g.) and acetoacetic ester (13 g.) were added, every second or third day, 10 c.c. of 1% sodium ethylate solution. After a fortnight the whole of the mixture was acidified with hydrochloric acid and extracted with ether. The acidified aqueous solution contained about 50-55% of the unchanged dimethylaminopropiophenone which could be recovered by making the solution alkaline with caustic soda.

From the residue of the ethereal extract, there appeared, after 24 hours, α-acetyl-γ-benzoylbutyric acid ester (I) which crystallised from alcohol in the form of colourless prismatic needles, yield 2·3 g.

$$Ph{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2 + MeCO{\cdot}CH_2{\cdot}CO_2Et \longrightarrow (I) + NH(CH_3)_2$$

By the distillation of the oily portion in vacuum at 12 mm. the following fractions were obtained:—

(*i*) till 100° (5 g). Raw material, *e.g.*, acetoacetic ester.

(*ii*) 200-205° (6·5 g.). When allowed to stand for a week or so there appeared crystals of phenyl*cyclo*hexenone (III). The oily portion consisted of phenyl*cyclo*hexenonecarboxylic acid ester (II).

(*iii*) 300° (0·5g.). Polymerised phenylvinylketone.

Ethyl α-acetyl-γ-benzoylbutyric acetate was obtained by the method (*b*) in the form of prismatic needles from alcohol, m.p. 120°. (Found: C, 68·54; H, 7·0. $C_{15}H_{18}O_4$ requires C, 68·68; H, 6·92 per cent).

On heating this ester at 200° for 2 hours, alcohol and CO_2 were given off and from the residue phenyl*cyclo*hexenone was obtained by crystallisation from petrol ether, m.p. 64°

Monoxime.—A solution of diketonic acid ester (I) (0·5 g.) in alcohol (15 c.c.), was mixed and heated on a water-bath with an

aquous solution of hydroxylamine hydrochloride (0·3 g.) and potassium acetate (0·4 g.). The insoluble oxime was crystallised from alcohol, m.p. 160-61°. (Found: N, 5·23. $C_{15}H_{19}O_4N$ requires N, 5·05 per cent).

4-Phenyl-6-keto-$\Delta^{4,5}$-cyclohexene-1-carboxylic acid ester (II) was obtained by the fractional distillation of the oily portion mentioned above under (*b*), b.p. 200-205°/12 mm. (Found: C, 74·03; H, 6·86. $C_{15}H_{16}O_3$ requires C, 73·75; H, 6·61 per cent).

Experiments performed in order to get the semicarbazone and *p*-nitrophenylhydrazone of this ester always resulted, even at low temperatures, in the saponification and splitting up of CO_2 and the formation of the corresponding derivative of phenylcyclohexenone.

5-Phenyl-$\Delta^{5,6}$-cyclohexenone-1 (III).—This was obtained through the saponification of phenylcyclohexenonecarboxylic acid ester (II). The ester was warmed for a short time with a little excess of an aqueous solution of *N*-KOH. The solution was acidified with hydrochloric acid and then extracted with ether. The residue on removing the solvent crystallised from petrol as prismatic leaflets, m.p. 64° (b.p. 172-73 /12 mm.). (Found: C, 84·06; H, 7·11. $C_{12}H_{12}O$ requires C, 83·69; H, 7·0 per cent).

In chloroform solution, it gave an addition product with a molecule of bromine, but it was not possible to crystallise the product.

The *oxime* was prepared by warming a solution of phenylcyclohexenone (0·5 g.) in alcohol (2 c.c.) with a concentrated aqueous solution of hydroxylamine hydrochloride (0·2 g.) and potassium acetate (0·3 g.) for 6 hours on a water-bath. It was crystallised from 50% alcohol as colourless crystals, m.p. 117-18°. (Found: N, 7·17. $C_{12}H_{13}ON$ requires N, 7·48 per cent).

The *semicarbazone* was prepared in the usual manner and crystallised either from alcohol or acetic acid, m.p. 222°. (Found: C, 68·07; H, 6·45; N, 18·17. $C_{13}H_{15}ON_3$ requires C, 68·10; H, 6·59; N, 18·34 per cent). The same semicarbazone was obtained from phenylcyclohexenone carboxylic acid ester (II).

The *p-nitrophenylhydrazone* was prepared in the usual manner and crystallised from alcohol in orange red prismatic crystals, m.p. 184-85°. (Found: N, 13·44. $C_{18}H_{17}O_2N_3$ requires N, 13·68 per cent).

Oxidation of phenylcyclohexenone through ozone.—The unsaturated ketone (III) (5 g.) was dissolved in dry chloroform (100 c.c.) and a fairly rapid current of ozone was allowed to bubble through the solution, till it became blue (8 hours), when the solid ozonide

crystallised out. After evaporating the chloroform, the ozonide was allowed to be decomposed by adding water (30 c.c.) and after 2 days, the solid crystals were sucked off and crystallised from hot water, m.p. 121°, and gave no depression with benzoic acid. The filtrate was shaken with ether in order to get rid of the dissolved benzoic acid. After evaporating the solvent the residue was crystallised from alcohol, m.p. 183° and gave no depression with succinic acid, yield succinic acid (2 g.) and benzoic acid (3 g.).

Polymerised phenylvinylketone.—The fraction obtained with b.p. 300°/12 mm. from the addition product of acetoacetic ester and phenylvinylketone was kept under petroleum for some days. The crystals thus separated were purified through crystallisation from alcohol, m.p. 108°. [Found: C, 81·93; H, 6·10. $(C_9H_8O)_x$ requires C, 81·78; H, 6·11 per cent).

1:5-*Diketo*-1:2:5-*triphenylpentane* (IV).—A solution of phenylvinylketone (1·4 g.) and desoxybenzoin (2 g.) in methyl alcohol (10 c.c) was treated with a concentrated solution of sodium methylate (0·05 g. sodium) under ice-cooling, when crystals separated which were recrystallised from methyl alcohol m.p. 97-98°, yield, 2·2 g. (Found: C, 84·27; H, 6·53. $C_{23}H_{20}O_2$ requires C, 84·11; H, 6·1 per cent).

The *monoxime* crystallised from a small quantity of alcohol, m.p. 125-26°. (Found: C, 80·59; H. 5·92; N, 4·36. $C_{23}H_{21}O_2N$ requires C, 80·70; H. 5·89; N, 4·09 per cent).

2:5-*Diphenyl*-$\Delta^{5:6}$-cyclo*hexenone*-1 (VII).—A solution of phenylvinylketone (6·5 g.) and benzylmethylketone (6·5 g.) in methyl alcohol (10 c.c.) was treated under ice-cooling with a concentrated solution of sodium methylate (1 c.c.) when a vigorous reaction ensued. The fraction obtained by distillation at 240 260°/12 mm. gave crystals, which were recrystallised from alcohol and a small quantity of acetic acid, m.p. 149 50° yield 20%. (Found: C, 87·34; H, 6·26 $C_{18}H_{16}O$ requires C, 87·05; H, 6·5 per cent).

2:5:6-*Triphenyl*-$\Delta^{5:6}$-cyclo*hexenone*-1 (VIII).—A solution of phenylvinylketone (6·5 g.) and dibenzylketone (10·5 g.) in methyl alcohol (10 c.c.) was treated under ice-cooling with a saturated solution of sodium methylate (1 c.c.) when a vigorous reaction ensued. The triphenyl*cyclo*hexenone which separated out was crystallised as prismatic needles from alcohol, m.p. 135°, yield 8 g. (Found: C, 88·71; H, 6·36. $C_{24}H_{20}O$ requires C, 88·84; 6·21 per cent).

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Denitrification in Sunlight and its Retardation.

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In the absence of oxygen and in presence of an easily oxidisable organic substance, many micro-organisms are capable of decomposing nitrates with the evolution of gaseous nitrogen or nitrous oxide or ammonia. This type of denitrification is well known and is one of the first microbiological changes to be investigated.

There is another variety of nitrogen loss, which takes place in presence of oxygen but has not yet been satisfactorily explained. In this paper it will be shown that this loss of nitrogen from the soil is due to an oxidation process followed by a photochemical and catalytic decomposition. This phenomenon of denitrification is of considerable importance as the loss of nitrogen in this process under certain conditions may be double the amount of nitrogen taken up by the plants grown on the soil.

From the researches of Lipman and Blair (*Soil Sci.*, 1921, 12, 1) it appears that nitrogen in the gaseous state is lost from soils when the conditions are favourable for oxidation. The loss amounted to 100 lbs. per acre per year in the first nine inches of the soil and after ten years the loss in New Jersey soil was 1000 lbs. per acre. In California the loss was 500 lbs. per acre in five years. In these experiments the conditions existing in the soil in the past were disturbed by making the soil suitable for more oxidation.

The following figures show the nitrogen loss due to the formation of gaseous nitrogen, in the experiments carried on in the California Experiment Station in the first five years

	Land with crops.	Land without crops.
Loss of nitrogen from 1600 lbs. soil ...	198 g.	124 g.
Nitrogen in crops	65	0
Net loss	133	124

Similar nitrogen losses have been observed at Rothamsted, (England), and the results are recorded below:—

Treatment.	Crop yield per acre per year. Grain Bushels.	Straw Cwt.	Recovered crop per year.	N as nitrate in drainage water parts per million.	N in soil.	N lost from soil, per year.
NH_4 salts containing 86 lbs. N + enough P & K salts	26·7	30·75	33·5 lb.	8·5	0·116%	51 lb.
No P or K salts	16·0	14·75	45·0	17·8	0·106	67·5

Loss of nitrogen has been observed by Shutt (*J. Agric. Sci.*, 1910, **3**, 335) on breaking for cultivation the prairie soil of the Indian Head, Saskatchewan.

Loss of nitrogen in top 8 *inches reported by* Shutt.

Nitrogen present in unbroken prairie	0·371%	6940 lb. per acre,
,, ,, after 22 years' cultivation	0·254%	4750
Loss from soil		2190
Recovered in crop		700
Loss in 22 years		1490
Loss per year		68

Marked loss of nitrogen has also been reported with Minnesota and Kansas soils. Nearly 70% of the added nitrogen is said to have been lost when wheat plots in Rothamsted, England, have received 14 tons of farm-yard manure containing 200 lbs. nitrogen per acre. These losses are more pronounced in soils, which have been highly aerated. From the foregoing observations it can be concluded that nitrogen loss can take place from well aerated soils provided the nitrogen content is high. Moreover, the following results show that this loss is high when the soil is wet and acidic.

Annett, Aiyer and Kayasth (*Mem. Dept. Agric. India, Chemical Series*, 1928, **9**, 155) have reported marked losses of nitrogen from a black cotton soil at Nagpur (India) during the heavy August rains, as they did not observe a corresponding gain in the drainage water. Moreover, Meggit (*ibid.*, 1923, **1**, 31) has observed great losses of nitrogen in the acid humid soil of Assam (India). Russell ("Soil Conditions and Plant Growth", 1932, pp. 367-69) has stated this problem of the nitrogen loss in the following words:—

"There is considerable difficulty in accounting for the nitrogen lost from the soil during the first 20 or 30 years of cultivation. It has, therefore, been supposed that nitrogen is evolved during the oxidation, and as all attempts to break off nitrogen from nitrate in these conditions have failed, it is assumed to come from the organic matter. This assumption involves the difficulty that no loss of nitrogen has been observed in the straightforward bacterial oxidation of organic substances such as albumin, asparagin or mixtures such as urine or faeces." "Yet somehow and somewhere gaseous nitrogen must be evolved to balance the considerable amount of fixation that is known to take place."

That oxidation of the ammonium salts is an important factor in this type of denitrification is also evident from the following observations. Ni klewski (*Rocz. Nauk. Roln.*, 1923, **9**, 1) reported the largest loss of nitrogen as a result of the influence of the nitrifying bacteria on stable manure. When the manure was free from nitrifying bacteria, only 3% nitrogen was lost as ammonia but when supplied with nitrifying bacteria, the manure lost more than 20% of its nitrogen. Moreover, Russell and Richards (*J. Agric. Res.*, 1917, **8**, 495) have observed a greater loss of nitrogen when a manure was composted under ærobic than under anærobic conditions as will be clear from Table I.

TABLE I.

	NH_3-N.	NO_3-N.	NO_2-N.	NH_3-N.	Other nitrogenous compounds (proteins).	Total.
			Anærobic conditions.			
Start	28%	0%	0%	8%	64%	100%
At 6° for 50 days	29	0	0	9	57	95
At 26° for 50 days	44	0	0	7	47	98
			Aerobic conditions.			
Start	33	0	0	8	59	100
At 15°	11	11	8	0	42	72
At 26°	5	2	7	0	55	69

Recently Viswanath (*Sci. Reports Dept. Agric. Madras*, 1930-31) has obtained greater nitrogen loss and greater velocity of oxidation in the nitrification of ammonium salts than with farm-yard or green manure.

Estimation carried on in different parts of the world especially at Rothamsted (England), Grignon (France) and other places in Europe, Ithaca (U. S. A), India and Egypt show that the total amount of nitrate present in soils with crop is less than that in neighbouring fallow soils even when correction is applied for the amount of nitrate taken up by the crop. Starkey (*Soil Sci.*, 1927, **27**, 319) has also reported that the velocity of nitrate production and evolution of CO_2 is greater in cropped than in fallow land. Table II shows the results obtained by Russell (*J. Agric. Sci.*, 1914, **6**, 18) regarding the influence of growing plants on the nitrate content of a soil.

TABLE II

	June, 1911.		July, 1912.	
	Fallow land.	Cropped land.	Fallow land.	Cropped land.
N as nitrate in first 18″ of soil ...	54	15	46	13
N in crop per acre ...	...	23	...	6
Total N in lb. per acre ...	54	38	46	19
Deficit in cropped land in lb per acre ...	...	16	...	27
	Expressed as nitrogen in parts per million.			
N as nitrate in 0 to 9″ depth ...	12	4	8	2
9″ to 18″ depth ..	9	2	10	3

From quantitative observations on the evolution of carbon dioxide from oxidation reactions taking place in the soil during the growth of plants, Neller (*Soil Sci.*, 1922, **13**, 139) concluded that much more rapid oxidation takes place in the soil with growing plants than in the uncropped soils under identical conditions.

Moreover, Burd (*J. Agric. Res.*, 1919, **18**, 51) has reported a substantial loss of nitrogen from the aerial parts of the barley plant during the period of translocation of materials in the second stage of the development of the plant.

Martin and Massey (*Wellcome Research Labs., Khartoum Chem. Pub.*, 1923, 29) working at Khartoum (Egypt) reported the disappearance of the nitrates from dry tropical soils.

Recently we have studied the loss of nitrogen when solutions of ammonium salts are exposed to sunlight and air for a long time in open beakers with or without photocatalysts. In order to determine the loss in the dark, similar experiments were carried on in beakers

kept in the dark. The following results showing the ammoniacal nitrite and nitrate nitrogen contents of the exposed and unexposed solutions were obtained when 100 c c. of 1% (with respect to ammonia) solutions of ammonium salts were exposed to sunlight for 350 hours.

TABLE III.

Amount of NH_3 originally present = 1 g.
,, ,, carbonate added = 1 g.
,, ,, ZnO or TiO_2 added = 5 gs.

	$(NH_4)_2SO_4$ alone.		$(NH_4)_2SO_4 + ZnO$.		$(NH_4)_2SO_4 + MgCO_3 + TiO_2$.	
	Light.	Dark.	Light.	Dark.	Light.	Dark.
NH_3	0·91	0·980	0·3856	0·460	0·6440	0·6528
NO_2 (Calc. as NH_3)	0·0002	0	0·0005	0·0004	0	0
NO_3 (Calc. as NH_3)	0·0032	0	0·0032	0	0·0035	0
Loss of Nitrogen (Calc. as NH_3)	0·0866	0·020	0·6107	0·5396	0·3525	0·3472

	$NH_4Cl + CaCO_3$		$NH_4Cl + CaCO_3 + TiO_2$		$NH_4Cl + MgCO_3 + ZnO$.	
	Light.	Dark.	Light.	Dark.	Light.	Dark.
NH_3	0·6354	0·7100	0·6879	0·6922	0·224	0·3286
NO_2	0·0002	0·0	0·0	0·0001	0·0003	0·0003
NO_3	0·0478	0·0	0·0032	0·0	0 0040	0·0
Loss of N	0·3168	0·2900	0·3089	0·3077	0·7717	0·6711

	$(NH_4)_2HPO_4 + TiO_2$.		$(NH_4)_2HPO_4 + CaCO_3 + TiO_2$.		$(NH_4)_2HPO_4 + MgCO_3 + TiO_2$.	
	Light.	Dark.	Light.	Dark.	Light.	Dark.
NH_3	0·5870	0·7054	0·4184	0·6220	0·3768	0·4250
NO_2	0·00025	0·0003	0·0004	0·0003	0·0020	0·0006
NO_3	0·0040	0·0	0·0041	0·0	0·0021	0·0
Loss of N	0·4065	0·2943	0·5771	0·3777	0·6191	0·5744

In these experiments, the open beakers containing the ammonium salt solutions with or without the photocatalysts and carbonate were

exposed to sunlight five days a week for 5 hours a day. After the completion of the experiments, the ammonia, nitrite and nitrate contents of all the solutions were estimated. In the foregoing tables, in order to obtain comparable results, the nitrite and nitrate contents of the solutions have been expressed in terms of ammonia.

The foregoing results show that the loss of nitrogen on exposing ammonium salt solutions to light and air is always greater in light than in the dark. In presence of zinc oxide and magnesium carbonate the loss is greater than with calcium carbonate, because more of free ammonia escapes due to the greater alkalinity of the medium containing zinc oxide or magnesium carbonate. The loss of nitrogen from all these solutions cannot be due only to the escape of ammonia from the solutions due to the alkalinity of the medium. The solutions in the beakers containing the ammonium sulphate alone and ammonium phosphate and TiO_2 were distinctly acidic from the beginning and hence in these beakers there was no appreciable loss of nitrogen as ammonia. Moreover, the beakers containing ammonium chloride and calcium carbonate showed alkaline reaction in the beginning and acidic reaction after the end of the exposure, whilst the solutions in the beakers kept in the dark were alkaline throughout. Similar results showing increased acidity after exposure were observed with the other reaction mixtures. These results show that a part of the ammonium ion was replaced by the acidic nitrite and nitrate ions on exposure to light due to the photo-oxidation of the ammonium salts. A part of the ammonium nitrite produced in this way seems to be decomposed into nitrogen and water and that is why in all beakers even in the ones containing acidic solutions from the very beginning, there is greater loss of nitrogen in the exposed than in the unexposed solutions.

In order to throw further light on this problem, we have carried several experiments by exposing solutions of ammonium chloride mixed with sodium nitrite of different concentrations in presence of TiO_2, Fe_2O_3, ZnO, sterilised and unsterilised soils. The total volume of the solutions was made up to 50 c.c. and exposed to sunlight in open beakers for about 7 hours every day. After the necessary exposure to light, the ammoniacal nitrogen, nitrite nitrogen and the nitrate nitrogen of the solutions were estimated. In some of the experiments the influence of the addition of cane sugar has also been investigated. The results obtained with sterilised and unsterilised soils are recorded in the following tables.

TABLE IV.

Exposure to sunlight from 7th October to 20th November, 1934. Total exposure = 77 hours.

	N added as NH_3	N added as nitrite.	Total N added.	Ammoniacal N left	NO_3-N left.	NO_3-N formed.	N lost.	N lost.
10 g. unsterilised soil	0·14 g.	0·0138 g.	0·1538 g.	0·0933 g.	0·00912 g.	0·00012 g.	0·0513 g.	33·3 %
,, sterilised ,,	0·14	0·0138	0·1538	0·0789	0·00712	0·00053	0·673	43·6
,, unsterilised ,, + 0·3 g. cane sugar	0·14	0·0138	0·1538	0·0986	0·011	0·00001	0·0442	28·6
,, sterilised ,, + 0·3 g. cane sugar	0·14	0·0138	0·1538	0·0920	0·0081	0·00002	0·0537	34·9
,, unsterilised ,, + 1g. cane sugar	0·14	0·0138	0·1538	0·103	0·011	0	0·0398	25·7
,, sterilised ,, + 1 g. cane sugar	0·14	0·0138	0·1538	0·090	0·0092	0	0·0546	35·6
,, unsterilised ,,	0·14	0·0514	0·1914	0·070	0·0321	0.00071	0·0886	46·2
,, sterilised ,,	0·14	0·0514	0·1914	0·063	0·0292	0·00092	0·0983	51·6
,, unsterilised ,, + 0·3 g. cane sugar	0·14	0·0514	0·1914	0·0801	0·0438	0·00002	0·0675	35·1
,, sterilised ,, + 0·3 g. cane sugar	0·14	0·0514	0·1914	0·080	0·0422	0·00008	0·0691	36·1
,, unsterilised ,, + 1 g. cane sugar	0·14	0·0514	0·1914	0·0812	0·0441	0	0·0661	34·5
,, sterilised ,, + 1 g. cane sugar	0·14	0·0514	0·1914	0·080	0·0412	0	0·0702	36·6
10 g. unsterilised ,,	0·14	0·138	0·278	0·0375	0·0521	0·0021	0·1863	67·0
,, sterilised ,,	0·14	0·138	0·278	0·0333	0·0460	0·0052	0·1930	69·4
,, unsterilised ,, +0·3 g. cane sugar	0·14	0·138	0·278	0·0421	0·0981	0·00003	0·1382	49·6
,, sterilised ,, +0·3 g. cane sugar	0·14	0·138	0·278	0·0373	0·0559	0·00012	0·1848	66·4
,, unsterilised ,, +1 g. cane sugar	0·14	0·138	0·278	0·0466	0·0992	0	0·133	47·8
,, sterilised ,, +1 g. cane sugar	0·14	0·138	0·278	0·0412	0·0592	0	0·1784	64·1

TABLE V.

Exposure to sunlight from 30th July to 5th September, 1934. Total exposure = 72 hours.

		N added as ammonia.	N added as nitrite.	Total N added.	Ammoniacal N left.	NO_2-N left.	NO_3-N formed.	N lost.	N. lost.
1 g.	sterilised soil	0·014 g.	0·014 g.	0·028 g.	0 g.	0·00049 g.	0·0053 g.	0·0223 g.	79%
,,	unsterilised ,,	0·014	0·014	0·028	0	0 00082	0·0027	0·0255	90
2 g.	sterilised ,,	0·028	0·028	0·056	0	0·00125	0·0056	0·050	89
,,	unsterilised ,,	0·028	0·028	0·056	0	0·00145	0·00376	0·052	93
4 g.	sterilised ,,	0·056	0·056	0·112	0	0·00464	0·0035	0·104	92
,,	unsterilised ,,	0·056	0·056	0·112	0	0·00488	0·0026	0·105	93
8 g.	sterilised ,,	0·112	0·112	0·224	0·000336	0·00586	0·008	0·211	94
,,	unsterilised ,,	0·112	0·112	0·224	0·000312	0·00688	0·0073	0·210	94

TABLE VI.

Exposure to sunlight from 10th September to 5th October, 1934. Total exposure = 64 hours.

30 g. unsterilised soil	0·42 g.	0·42 g.	0·84 g.	0·138 g.	0·055 g.	0·017 g.	0·63 g.	75%
,, ,, ,, +5 g. cane sugar	0·42	0·42	0·84	0·200	0·411	0	0·229	27
,, unsterilised soil	0·42	0·315	0·735	0·155	0·0325	0·005	0·5425	74
,, ,, ,, +5 g. cane sugar	0·42	0·315	0·735	0·165	0·289	0	0·281	30

The foregoing results show that in all the solutions, there is a marked loss of nitrogen on exposure to sunlight due to the decomposition of ammonium nitrite. It is of great interest to note that the loss is less marked with dilute solutions of ammonium nitrite than in the stronger solutions when the weight of the soil is the same and the addition of cane sugar considerably retards this nitrogen loss and nitrate formation. Moreover, the results show that the decomposition of ammonium nitrite is greater, the greater the intensity of the light, the loss is greater in August and September than in October and November.

These observations on nitrogen loss in presence of air recorded in the foregoing pages which are unaccountable from the bacterial viewpoint (*vide* Russell's quotation on page 69) are explained from the following considerations.

The soil invariably contains some ammonium salts mainly as a result of the oxidation of the amino acids set free from its proteins. By the process of nitrification caused by light or bacteria the ammonium salts are first oxidised to nitrite. In other words, ammonium nitrite may be produced in the soil when a supply of air and light or nitrifying bacteria are available. Some years ago Dhar (*Proc. K. Akad. Wetensh. Amsterdam*, 1920, **23**, 308) observed that solutions of ammonium nitrite decompose into nitrogen and water when exposed to sunlight and this photochemcal decomposition is facilitated by acids and different solid surfaces. Our experiments by exposing solutions of ammonium salts and sodium nitrite to sunlight mixed with sterilised soil or unsterilised soil recorded in Tables IV, V and VI show marked decomposition of the ammonium nitrite in light. In presence of TiO_2, ZnO, Fe_2O_3, etc., the photo-decomposition of ammonium nitrite has also been observed. In several of these experiments specially in the stronger solutions and in the absence of sugar, copious evolution of gaseous nitrogen has been noted. Similar decomposition of ammonium nitrite formed temporarily in the soil from the processes of ammonification and nitrification is likely to take place in nature specially in humid soils. This decomposition of ammonium nitrite in the soil will be more evident when virgin or prairie soils are ploughed for cultivation. The organic nitrogenous compounds present in the soil have a chance to be oxidised first to ammonia and then to nitrite and finally to nitrate by the increase of aeration effected by ploughing. It seems that in the soil, normally the processes of ammonification and nitrification can go on simul-

taneously and thus at a certain stage in the processes of oxidation, ammonium nitrite may be generated and this being an unstable substance specially in presence of light and the soil surface acting as a catalyst, will partially decompose with the liberation of gaseous nitrogen. Moreover, when the nitrogenous manure is in large amounts and there is sufficient aeration, the possibility of the formation of the easily decomposable ammonium nitrite is increased and there is partial decomposition of this substance from soils receiving large amounts of farm-yard manures or ammonium salts. For the production of ammonium nitrite in the soil, aeration is necessary and that is why Russell and Richards observed more marked loss of nitrogen in ærobic than in anærobic conditions in composting as already reported. In tropical countries the decomposition of ammonium nitrite formed in the soil is likely to be marked because of the high temperature and strong sunlight; like sunlight, high temperature also facilitates the decomposition of ammonium nitrite.

The observation of Niklewski (*loc. cit.*) that there is more loss of nitrogen from stable manure in presence of nitrifying bacteria than in their absence, is also clear from the foregoing lines. As bacterial nitrification is an oxidation phenomenon, the ammonium salts in the manure are to a larger extent oxidised to nitrite when nitrifying bacteria are added to the manure than in their absence. Hence in the presence of the nitrifying bacteria, there is the possibility of the formation and decomposition of larger amounts of ammonium nitrite than in the absence of the bacteria. The observations of Viswanath showing greater oxidation and greater nitrogen loss with ammonium salts on nitrification than with farm-yard and green manures, can be easily understood from the view point advanced in this paper. As these experiments were carried on under field conditions, the photochemical and catalytic decomposition of a part of the ammonium nitrite and nitrous acid formed was possible.

It has been already stated that in cropped soils there is more nitrogen loss than in uncropped soils under the same conditions. This is due to the fact that there is more oxidation taking place in soils with growing crops than in fallow lands. This behaviour has been observed in different stations all over the world and is explicable from the view point of the partial decomposition of ammonium nitrite produced in the soil even for a short time. In the process of nitrification, the basic ammonium ion is replaced first by the acidic nitrite ion and finally by the nitrate ion and hence the acidity of the

soil undergoing nitrification is increased. Moreover, it has been already stated that the decomposition of ammonium nitrite is facilitated by acids and hence in soils not containing calcium carbonate, the loss of nitrogen in this manner will be marked.

It is well known that the soil-nitrogen cannot be increased alone without a corresponding increase in its carbon content. This leads to the interesting conclusion that in presence of carbonaceous matter, the soil-nitrogen is protected, because the carbonaceous matter acts as a negative catalyst and retards the process of nitrification which is an oxidation reaction. Unless nitrification takes place and nitrite ion is formed in place of ammonium ion, the formation and decomposition of ammonium nitrite are not possible. Hence in presence of large amounts of carbonaceous matter, this type of loss of nitrogen, would not be pronounced. Our experiments recorded in Tables IV and VI show that the addition of cane sugar markedly decreases the nitrate formation and loss of nitrogen from solutions containing ammonium and nitrite ions. On the other hand, in the absence of carbonaceous matter, the soil nitrogenous compounds will undergo oxidation more readily than in the presence of carbonaceous substances with the formation of ammonium nitrite, which is liable to be partially decomposed in the soil with consequent loss of nitrogen. From this point of view, the observations of Viswanath that there is greater oxidation and loss of nitrogen when ammonium salts are allowed to nitrify than with farm yard and green manures are easily explained. In the latter group of manures, along with nitrogenous compounds, there are carbonaceous compounds like cellulose, carbohydrates, fats, etc., which acting as negative catalysts markedly retard the oxidation of the proteins, amino acids and ammonium salts to nitrite and nitrate and hence in presence of cellulose, carbohydrates, fats, etc., added with farm yard and green manures, there is less oxidation of ammonim salts to nitrite and hence less chance for the formation and decomposition of ammoniuum nitrite. In several publications from these laboratories (*cf.* Dhar " New Conceptions in Biochemistry, 1932 pp. 44-45), it has been shown that both carbohydrate and fats markedly act as negative catalysts and retard the oxidation of amino acids and proteins and that is why carbohydrates and fats act as protein sparer in the animal body. Similarly in the soil, carbonaceous substances like cellulose, carbohydrates, fats, etc., added with organic manures retard the oxidation of proteins, amino acids, and ammonium salts by air and thus act as protectors

of the soil nitrogen compounds. It is clear, therefore, that when the carbon content of a soil is high and the nitrogen content low, there will be less oxidation of the soil nitrogen and less chance for the formation and decomposition of ammonium nitrite and less nitrogen loss than when the carbon content is low and nitrogen content high. The foregoing observations justify the application of organic manures for preserving the nitrogen of soils, specially in tropical countries, where due to sunlight and high temperature, the velocity of the oxidation of the soil organic and inorganic compounds is high and the nitrogenous compounds want more protection than in temperate climates.

Molasses from sugar factories in India are practically wasted now. They should be added to the soil for the fixation of atmospheric nitrogen as has been observed by us and for the preservation of the soil nitrogen compounds by decreasing their too rapid oxidation Of course too little oxidation of the protein present in the soil by the addition of molasses will not make the soil suitable for the growth of crops. It seems necessary that an equilibrium should be established between the oxidised and the unoxidised proteins, ammonium salts and other nitrogenous compounds, which are present in the soil for maintaining its fertility at a proper level. Too much oxidation of the nitrogenous substances and ammonium salts may entail marked nitrogen loss by this type of denitrification, and too little oxidation will not make the soil fertile enough for a good yield of crop. Hence the molasses should not be added in very large amounts and after the addition of molasses, the soil should be ploughed several times to help oxidation. In our field experiments at Allahabad, we have observed that the ammonia content of a garden soil is increased ten times by the addition of molasses in the ratio one part of molasses in 100 parts of soil and the soil is well aerated. If the soil is properly aerated by ploughing, molasses added in moderate amounts should prove to be a valuable fertiliser, specially in tropical countries. Moreover, the observation of Lipman and Blair (*loc cit.*) that nitrogen is lost from cropped soils inspite of added nitrogenous fertilisers is explained, because of the absence of the requisite amount of carbonaceous substances for the preservation of the nitrogenous compounds of the soil, the soil nitrogenous compounds are oxidised too rapidly forming ammonium nitrite (*cf.* Dhar, *J. Indian Chem. Soc.*, 1934, **11**, 883).

The experiments carried on in presence of cane sugar show that

the loss of nitrogen in the solutions containing sugar is much less than in the other beakers without sugar. The greater the sugar added, the greater is the retardation of the decomposition. Both the ammoniacal and nitrite nitrogen remaining in the beakers after exposure are greater in the presence of sugar than in its absence and this behaviour is more marked with the unsterilised than with the sterilised soils. It seems that in presence of sugar along with the retardation of the decomposition of ammonium nitrite, nitrogen fixation may take place and thus the apparent loss of nitrogen is less. We have observed nitrogen fixation as ammonia increment in soils when exposed to light in presence of cane sugar. Further work on the decomposition of dilute solutions of ammonium nitrite and the influence of sugars on this decomposition and nitrogen fixation is in progress.

From our experiments we find that the decomposition of ammonium nitrite is easy when a moderately strong solution containing ammonium and nitrite ions are exposed to light and this decomposition is favoured by acids. Our results recorded in Table IV, show that the nitogen loss is less in dilute solutions than in strong solutions. It seems that Barritt (*Biochem. J.*, 1931, **25**, 1965) did not observe the decomposition of ammonium nitrite, because his solution was not exposed to light and was dilute and the temperature of the solution low. A mixture of an ammonium salt and a nitrite in the solid state does not decompose appreciably in sunlight. In the soil under ordinary conditions, when unmanured, this decomposition is not much, because the soil is dry and the amount of ammonia being usually small, the quantity of ammonium nitrite formed is still smaller, and its decomposition is not expected to be high. Under normal circumstances, this type of denitrification should be observed more readily when large amounts of nitrogenous compounds are added to the soil or new soils are broken up for cultivation specially in warm and humid climates but when the soil nitrogen is small due to repeated cultivation without any addition of manure, this loss is likely to be slight.

In the experiments of Dhar, Bhattacharyya, and Biswas (*J. Indian Chem. Soc.*, 1933, **10**, 699) on the photonitrification of ammonium salts, the soil was kept very dry most of the time and the amount of ammoniacal nitrogen added was small, hence the possibility of the decomposition of the ammonium nitrite formed by oxidation of the ammonium salt was not high. The nitrite is also oxidised to nitrate, which is stable in light.

Under certain circumstances, the soil nitrate may be reduced to nitrite by the organic substances in the soil possibly with the simultaneous formation of organic acids. In this way there is also the possibility of the generation of ammonium nitrite and nitrous acid and their decomposition and consequent loss of nitrogen. The formation of nitrite from nitrate has been suspected by Nagaoka (*Bull. Coll. Agric. Tokyo*, 1904, **6**, No. 3, 285), Daikuhara and Imaseki (*Bull. Imp. Centr. Agric. Expt. Sta. Japan*, 1907, **1**, No. 2, 7), in the Japanese swampy rice fields, by Keley (*Hawaii Agric. Exp. Sta. Bull.* 1911, 24) in Hawaii and by Sen (*Proc Imp. Council Agric. Res.*, 1933) in Bengal (India). It is well known that there are numerous micro-organisms in the soil capable of reducing nitrate to nitrite in presence of reducing substances like peptone, glucose, glycerol, carbohydrates. Many aerobic micro-organisms can act anærobically in the presence of nitrate.

Moreover, partial loss of nitrogen from the soil is possible from the decomposition of nitrous acid according to the equation,

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

The nitrite formed either by the oxidation of ammonia or by the reduction of nitrate may be easily converted into nitrous acid by the acids, which may be present in the soil because nitrous acid is a comparatively weak acid (dissociation constant $= 4 \times 10^{-4}$). Even carbonic acid slowly decomposes nitrites, as nitrous acid itself is unstable and decomposes into nitric acid and nitric oxide, which may escape in the gaseous condition. It seems that the decompositions of ammonium nitrite and nitrous acid will be more pronounced in solutions than in dry soil and thus the observations of Meggitt (*Mem. Dept. Agric. India*, 1923, **7**, 31) on great losses of nitrogen in the acid humid soil in Assam (India) may be explained. There is also the possibility of the reaction of nitrous acid on amines, amides, and amino acids which may sometimes be formed in the decomposition of soil organic substances.

Summary.

1. The researches of different investigators show that nitrogen in the gaseous state is lost from soils when the conditions are favourable for oxidation. The loss of nitrogen in this process may be double the amount of nitrogen taken up by the plants grown on the soil.

2. A greater loss of nitrogen is observed when a manure is composted under ærobic than anærobic conditions. Moreover, when there is a large amount of carbonaceous matter present in the manures along with nitrogenous compounds, the velocity of the oxidation of nitrogenous compounds and the amount of nitrogen loss are also decreased.

3. Experiments carried on at different places show that the total amount of nitrate present in soils containing crops is less than that in neighbouring fallow soils even when a correction is applied for the amount of nitrate taken up by the crop. The oxidation processes are more vigorous in soils with crops than in those without them.

4. Our experimental results show that the loss of nitrogen on exposing ammonium salt solutions to light and air is always greater in light than in the dark. Moreover, solutions of ammonium chloride and sodium nitrite decompose readily with evolution of nitrogen when exposed to sunlight in open beakers mixed with sterilised and unsterilised soils. This decomposition is considerably less in dilute solutions of ammonium nitrite and also when cane sugar is added to the solutions containing ammonium and nitrite ions.

5. All these observations have been explained from the view point that in the processes of ammonification, and nitrification taking place in the soil or in solutions, ammonium nitrite is produced. Ammonium nitrite has been found to be decomposed into nitrogen and water readily by increase of temperature or exposing it to light. The formation of ammonium nitrite from ammonium salts or proteins requires oxygen and that is why, this type of denitrification is facilitated by increased soil aeration and also soil acidity, as nitrous acid also undergoes decomposition.

6. Addition of carbonaceous substances like molasses tends to preserve the soil nitrogen by decreasing the velocity of the oxidation of the nitrogenous compounds present in the soil and thus decreasing the probability of the formation and decomposition of ammonium nitrite. Moreover, molasses, when added to soil in moderate amounts and the soil is properly aerated for helping the oxidation reactions, cause nitrogen fixation as evidenced by the increase of ammoniacal nitrogen of soil.

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Action of Dyestuffs and Narcotics on Proteolytic Enzymes. Trypsin and Papain.

By Kalipada Basu and Ramakanta Chakravarty.

The purification of many enzymes has reached a very high stage and in the case of some enzymes like urease (Summer, *J. Biol. Chem.*, 1926, **69**, 435) and pepsin (Northrop, *J. Gen. Physiol.*, 1930, **13**, 739, 767), it is claimed that they have been obtained in the pure crystalline form. But very little is known about the constitution of the enzymes. An insight into the constitution and mode of action of the enzymes could be obtained if the nature of the active group or groups in the enzyme could be determined. Toxic actions of substances of known structure on an enzyme would give us some information about the nature of the active group in the latter. Investigations in this line have been begun by Bamann and Schmeller (*Z. physiol. Chem.*, 1931, **194**, 1) who showed that indicators of the type phenolphthalein, bromothymol blue, etc., have a toxic action on lipase. Quastel (*Biochem. J.*, 1931, **25**, 628, 898; 1932, **26**, 1685) has tried the action of a series of acidic and basic dyes on dehydrogenase, fumarase and urease, and finds that generally the inhibiting action of the dyestuffs is limited to the basic dyestuffs. It should thus be possible to distinguish between apparently closely related enzymes like the different proteinases, polypeptidases, etc., by taking advantage of the specific toxic action of the dyestuffs.

The first observation on the action of dyestuffs on proteolytic enzymes was made by Marston (*Biochem. J.*, 1923, **17**, 851) who found that dyes of the safranine type precipitated the proteolytic enzymes, the precipitates being proteolytically active.

The purpose of the present investigation is to attempt to elucidate the nature of the proteolytic enzymes, trypsin and papain, by trying the action of a large number of basic and acidic dyestuffs and also of some narcotics.

Experimental.

It is known that the hydrolytic action of the enzymes, trypsin and papain consists in the breaking up of the $-CO-NH-$ linkage and the amount of hydrolysis was determined by estimating the amino-nitrogen with the micro-Van Slyke apparatus.

The method was to determine the amount of hydrolysis in certain periods produced by a definite weight of the enzyme in a substrate (like peptone) and to compare this with the amount of hydrolysis produced by the same weight of the enzyme after the latter had been exposed to the action of a dyestuff at a concentration of 1/2000 or of a narcotic at a concentration of 1/4000 for an hour. The concentration of the dyestuff was 1/5000 and of the narcotic 1/10,000 in the reaction vessel.

The action of a large number of acidic and basic representative dyestuffs from different series has been tried. The names of the dyes are given in the relevant tables.

The Inhibiting Action of Dyestuffs on Trypsin.

The enzyme material was a preparation of pancreatic trypsin by Messrs. Carnick & Co., U.S.A., that is known by the name of "Trypsogen". Cystin, neutralised and brought up to the desired p_H, was used throughout as an activator (*cf.* Grassman, *Z. physiol. Chem.*, 1930, **186**, 183). Phosphate buffer (p_H8·67) was used in these experiments.

0·2 G. of trypsogen dissolved in water and 0·06 g. of cystin dissolved in a minimum quantity of NaOH solution and brought to the desired p_H (8·67) with HCl solution were transferred to a 25 c.c. measuring flask. 2 C.c. of phosphate buffer of p_H 8·67 and 2 c.c. of the dye solution were also added to the flask. The concentration of the dyestuff in the flask was now 1/2000. The measuring flask was then allowed to stay for an hour in a thermostat at a temperature of 37° so that the enzyme was subjected to the action of dyestuff After this period 5 c.c. of a peptone solution that was previously brought up to p_H 8·67 were added quickly to the measuring flask and the volume made up to 25 c.c. with water. The concentration of the dyestuff was now 1/5000. 4% Solution of the peptone was used. This peptone solution and water were also kept in the thermostat to acquire the same temperature as the solution, *i.e.*, 37°. Now 2 c.c. of the solution were withdrawn from the flask and allowed to run into the reaction chamber of a micro-Van Slyke apparatus and the NH_2-nitrogen determination made in the usual way (Van Slyke, *J. Biol. Chem.*, 1915, **23**, 407). The volume of the nitrogen in the burette was noted. The measuring flask with the solution was kept in the thermostat at the same temperature and a second Van Slyke

determination with 2 c.c. was made after 30 minutes of the first determination. A third determination was made after an hour.

Blank experiment was done without the dyestuff and this blank determination was made from time to time in order to see that the activity of the enzyme remained practically identical and also to take into account the slight changes in activity from time to time. The results obtained are summarised in Table I.

TABLE I.

Percentage inhibition of hydrolysis of peptone with trypsin by different dyestuffs.

$p_H = 8{\cdot}67$. Temp. = 37°.

Basic dyestuffs (1/2000).	% Inhibition.	Basic dyestuffs (1/2000).	% Inhibition.
Brilliant green	18	Toluidine blue	35
Malachite green	0	Janus green	6
Methyl violet	19	Neutral red	0
Crystal violet	0	Chrysoidin	26
Ethyl violet	20	Pyronine	19
Gentian violet	0	Methylene violet	22
Bismarck brown	16	Safranine	0
Methylene blue	0	Auramine	28
Acid dyestuffs (1/2000).	**% Inhibition.**	**Acid dyestuff (1/2000).**	**% Inhibition.**
Erythrosin	26	Soluble blue	16
Eosin yellow	29	Congo red	33
Eosin bluish	28	Benzopurpurin	0
Acid green	20	Orange G.	6
Acid fuchsin	36	Cyanin chloride	11
Water blue	9	Heamotoxylin	30

Conclusion.—It would appear from above that some basic and all acidic dyestuffs are toxic to trypsin at p_H 8·67 and at a concentration of 1/2000. It must be observed, however, that the inhibition never exceeds 36% and in no case reaches 100% that was observed

in the case of the dehydrogenase, fumarase and urease studied by Quastel. It is reasonable to suppose that the inhibiting action of dyestuffs is due to their combination with the enzyme and the enzyme trypsin, therefore, must possess both acidic and basic groups and have amphoteric properties. In this, trypsin resembles fumarase on which both acidic and basic dyestuffs exert toxic action and differs from dehydrogenase and urease whose action is inhibited by basic dyestuffs alone (Quastel, *loc. cit.*).

There is, however, a marked specificity in action both among the acidic and basic dyestuffs and dyestuffs belonging to the same series act in quite different ways. Thus of the basic dyestuffs of the triphenylmethane series, malachite green, crystal violet and gentian violet exert no toxic action, while brilliant green, methyl violet, and ethyl violet inhibit almost to the same extent. The acid dyestuffs of the triphenylmethane series (acid green, acid fuchsin, water blue, soluble blue) are all toxic. Methylene blue is inert while toluidine blue exerts the highest toxic action amongst the basic dyestuffs. Safranine is, as was found by Marston, inert but methylene violet is toxic. Similar behaviour was also observed by Quastel in his investigations, who found, for instance, neutral red inert but Janus green toxic, orange G. inert but congo red highly toxic towards fumarase.

It will thus be seen that the *structure* of the dyestuff molecule is also an important factor in determing its toxic action.

Dyestuffs and Proteolytic Action of Papain.

Papain differs from trypsin in having a p_H optimum ($p_H 5{\cdot}0$) quite different from that of trypsin. The action of all the above dyestuffs was tried on papain. Experiments were done both with Merck's papain (Succus caricae Papayae Siccatus) and also with a sample of papain prepared by us from the fresh milky juice of the carica papaya. This was done by extracting the dried juice with water, centrifuging and precipitating the clear liquid with alcohol. The precipitate was freed from alcohol and was found to be about three times more active than the Merck's preparation.

The activation of the enzyme was affected by cystein, cystin being inert in this case (*vide*, Grassmann, *loc. cit.*). The reaction was carried at p_H 5·0. Gelatine was used as the substrate.

0·2 G. of Merck's papain was taken. A 0·1*M* solution of cystein was prepared and 1 c.c. of the solution was added to the papain solu-

tion for activation. Citrate buffer (p_H 5·0) was used. The cystein solution was brought to the same p_H by adding alkali solution in drops. The solution of papain, cystein (1 c.c.) and the dyestuff (2 c.c.) were taken in a 25 c.c. measuring flask and the mixture was allowed to remain for an hour in the thermostat at 37°. The concentration of the dyestuff was 1/2000. Just before the reaction, 10 c.c. of a 3% gelatine solution at p_H 5·0 was added to the measuring flask and the volume was made up to 25 c.c. with water, the temperature of water and gelatine being also 37°. The concentration of the dyestuff was now 1/5000, 2 c.c. of the mixture were withdrawn and analysed in the Van Slyke apparatus. A second determination was made after an hour of the first reaction. The final determination was made after 2 hours. In the case of laboratory prepared papain 0·08 g. was taken in each reaction. The results obtained are summarised in Table II.

TABLE II.

Percentage inhibition by dyestuffs of gelatine hydrolysis by papain.

p_H=5 0. Temp.=37°.

Basic dyestuff. (1/2000)	% Inhibition Merck's papain.	% Inhibition Prepared papain.	Basic dyestuff. (1/2000)	% Inhibition Merck's papain.	% Inhibition Prepared papain.
Brilliant green	5	6	Toluidine blue	6	4
Malachite green	1	3	Janus green	17	5
Methyl violet	4	4	Neutral red	4	2
Ethyl violet	11	2	Chrysoidin	25	9
Gentian violet	1	6	Pyronin	3	2
Bismarck brown	3	4	Methylene violet	9	4
Methylene blue	6	3	Safranin	1	3
			Auramin	6	2
		Acid dyestuffs (1/2000)			
Erythrosin	26	16	Soluble blue	9	6
Eosin yellow	5	3	Congo red	18	1
Eosine bluish	13	6	Benzopurpurin	13	12
Acid green	1	6	Crystal scarlet	5	16
Acid fuchsin	5	9	Orange G.	12	2
Water blue	2	4	Cyanin chloride	12	6
			Haemetoxylin	7	6

The above table makes it clear that as in the case of trypsin both acidic and basic dyestuffs are toxic showing the amphoteric nature of papain. The same specificity of action amongst dyestuffs of the same series is to be observed here. Thus Janus green is fairly toxic while neutral red is inert. Here again the importance of the structure of a dyestuff in determining its toxic action is apparent.

One fact, however, forces itself upon our observation. The dyestuffs appear to be less toxic towards the purer laboratory preparation of papain than towards the less active and therefore, less pure Merck's papain. Similar observations have been made by Quastel (*Biochem J.*, 1932, **26**, 1683) in his study of the action of dyestuffs on urease. It is possible that some substance is present in Merck's preparation, which enhances the toxicity of the dyestuffs.

Crystal scarlet alone is more toxic towards the purer preparation. Quastel also found neutral red and Janus green more toxic towards the purer urease.

The Action of Narcotics on the Proteolytic Enzymes, Trypsin and Papain.

Although there are some observations on the effect of narcotics on the Schardinger enzyme and succinic dehydrogenase by Sen (*Biochem. J.*, 1931, **25**, 849) and on brain dehydrogenose by Quastel (*ibid.*, 1932, **26**, 1672) no data are available on the action of narcotics on proteolytic enzymes. The inhibiting effect of narcotics on enzymic reactions is supposed to be due to the preferential adsorption of these substances on enzyme surfaces and the reaction velocity is diminished owing to the displacement of the substrates from the enzyme surface by the narcotics (Warburg, *Biochem. Z.*, 1921, **119**, 134).

The action of the narcotics, diethylurea, ethyl urethane, phenyl urethane, vanillin and also of the following substances, catechol, pyrogallol, gallic acid and sodium hydrosulphite on trypsin and papain has been tried in order to find out if it might throw some light on the nature of the enzymes.

Carnrick's "Trypsogen" and papain prepared in the laboratory by us were employed. The same procedure was employed as in the case of the dyestuffs with the difference that the solution of the dyestuff was replaced by the same volume of a solution of the narcotic. The enzyme in presence of the activator was subjected to the action of the narcotic

at a concentration of 1/4000 for an hour and when finally the substrate solution was added and the reaction mixture was made up to 25 c.c., the concentration of the narcotic fell to 1/10,000. The results are as follows.

TABLE III.

Percentage inhibition by narcotics of peptone hydrolysis by trypsin.

p_H=8·67. Temp.=37°

Narcotic $\left(\frac{1}{4000}\right)$.	Percentage inhibition after 35 min.	65 min.
Pyrogallol	2	9
Ethyl urethane	0	8
Diethylurea	0	9
Vanillin	6	7
Gallic acid	0	10
Catechol	0	10
Phenyl urethane	0	0
Sodium hydrosulphite	0	7

TABLE IV.

Percentage inhibition by narcotics of gelatine hydrolysis by papain.

p_H=5. Temp.=37°.

Narcotic $\left(\frac{1}{4000}\right)$.	Percentage inhibition after 60 min.	120 min.
Pyrogallol	0	0
Ethyl urethane	5	5
Diethyl urea	0	0
Vanillin	0	9
Gallic acid	5	16
Catechol	0	0
Phenyl urethane	3	3
Sodium hydrosulphite	0	0

It will be observed that in the case of papain the narcotics are without any action, only gallic acid, vanillin and ethyl urethane causing some inhibition. The inhibiting action increases with time. In the case of trypsogen practically all the substances tried show no effect for the first hour of the reaction but an appreciable inhibiting action is to be noticed after two hours. This shows that the adsorption of the narcotics on trypsin surface is very slow and is inappreciable for the first two hours. Similar results were obtained by Quastel in the case of the action of Somnifaine on brain dehydrogenase.

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Bromination of Substances Containing two Aromatic Nuclei. Part I. Bromination of Cresyl and Nitrophenyl Benzoates.

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The object of the present work is to investigate the positions taken up by bromine on entering a molecule containing two aromatic nuclei. Kauschke (*J. pr. Chem.*, 1895, *ii*, **51**, 210) found that phenyl and cresyl benzoates are readily brominated but he did not establish the constitution of the products. In this work the cresyl esters are brominated according to the method of Kauschke (*loc. cit.*) and it is found that the use of fuming nitric acid (*d* 1·45) as a carrier, according to Varma and Pannicker (*J. Indian Chem. Soc.*, 1933, **10**, 500) is advantageous.

The constitution of the products has been established by hydrolysis and synthesis from the respective acid chloride and cresols. *o*-,*m*-, *p*-Cresyl benzoates yield respectively 4-bromo-2-methyl, 4-bromo-3-methyl- and 2-bromo-4-methylphenyl benzoates.

With nitrophenyl benzoates, the nitro group so deactivates its nucleus that bromine enters the acidic rings. Resistance to bromination is marked, so that the usual carriers are found ineffective, and reaction could be brought about only in presence of fuming nitric acid (*d* 1·45). *o*-, *m*-, *p*-Nitrophenyl benzoates yield the corresponding nitrophenyl *m*-bromobenzoate, when the reacting substances are in molecular proportion (1:1).

If the ester and bromine are used in molecular proportion of 1:2, *o*- and *m*-nitrophenyl benzoates yield the respective nitrophenyl 2:5-dibromobenzoates ; while the *para* isomer under these coditions yields only monobromo derivative. *p*-Nitrophenyl 2:5-dibromobenzoate can, however, be obtained by brominating *p*-nitrophenyl *m*-bromo benzoate.

The constitution of these esters has been established by hydrolysis.

Experimental.

4-Bromo-2-methylphenyl benzoate.—To a mixture of *o*-cresyl benzoate (8 g.) and bromine (6 g.), fuming nitric acid (*d* 1·45, 10 c.c.) was gradually added and the whole heated on a water-bath with a reflux condenser for about 4 hours. The mixture was diluted with water and neutralised with sodium carbonate when a solid separated. It crystallised from alcohol in cream coloured needles, m. p. 65°, yield 55%. It is soluble in common organic solvents. Kauschke (*loc. cit.*) gives m. p. 59°. (Found: Br, 27·4. $C_{14}H_{11}O_2Br$ requires Br, 27·5 per cent).

The mixed melting point of the ester with synthetic 4-bromo-2-methylphenyl benzoate (Jadhav and Rangwala, *Bombay Univ. J.*, 1934, 3, 161), showed no lowering.

Hydrolysis.—The bromo ester (4 g.) was boiled with alcoholic caustic potash solution (6 g. in 50 c. c.) for 10 hours. The solution was acidified and alcohol removed. The solid obtained was treated with sodium carbonate solution, the aqueous layer separated from the oil and acidified, when a solid separated. It was crystallised from hot water and identified as benzoic acid. The oil must, therefore, be 4-bromo-*o*-cresol.

4-Bromo-3-methylphenyl benzoate was prepared in the same way as the *o*-cresyl isomer, the mixture being heated for 8 hours. The paste obtained after dilution and neutralisation solidified on keeping in the refrigerator. It crystallises from alcohol in needles, m. p. 82-3°, yield 70%. (Found : Br, 27·3. $C_{14}H_{11}O_2Br$ requires Br, 27·5 per cent).

The mixed melting point of the bromo ester with authentic 4-bromo-2-methylphenyl benzoate (Walter and Zipper, *J. pr. Chem.*, 1915, 91, *ii*, 377) showed no lowering. Benzoic acid was obtained by the hydrolysis of the ester.

2-Bromo-4-methylphenylbenzoate.—Bromination was effected by heating the ester with bromine for 10 hours without fuming nitric acid, which did not improve the yield. The product is a thick oil which is difficult to distil. It solidifies below 0°, yield 60%. (Found: Br, 27·5. $C_{14}H_{11}O_2Br$ requires Br, 27·5 per cent).

The substance gave benzoic acid on hydrolysis and the crystalic portion had b. p. 219-21°. (Found: Br, 42·5. C_7H_7O Br requires Br, 42·8 per cent).

The boiling points for 2-bromo-*p*-cresol given in the literature are 218-20° (Henninger, *Ber.*, 1882, **15**, 1081); 213-14° (Schall and Dralle, *Ber.*, 1884, **17**, 2530; Stormer and Gohl, *Ber.*, 1903, **36**, 2875); 218-19° (Zincke and Wiederhold, *Annalen*, 1902, **320**, 203).

o-*Nitrophenyl* m-*bromobenzoate*.—To a mixture of *o*-nitrophenyl-benzoate (12 g.) and bromine (8 g.), fuming nitric acid (*d* 1.45, 20 c.c) was gradually added and the whole was refluxed for about 5 hours on a water-bath. The reaction product was poured into water and neutralised with sodium carbonate. The solid obtained crystallises from alcohol in cream coloured plates, m. p. 105°, yield 45 %. It is soluble in acetone, chloroform and benzene, sparingly so in carbon tetrachloride, alcohol and acetic acid. (Found: Br, 24·6. $C_{13}H_8O_4$ NBr requires Br, 24·8 per cent).

The ester was hydrolysed by boiling with aqueous caustic potash solution (about 20%) for 2 hours. The solution was acidified and *o*-nitrophenol was removed by steam distillation, and the acid, crystallised from the hot solution on cooling, melted at 155-156°. It was identified as *m*-bromobenzoic acid by mixed melting point with an authentic sample.

m-*Nitrophenyl* m-*bromo-benzoate* was prepared in the same way as the *o*-isomer. The solid obtained crystallises from acetic acid in white needles, m. p. 132°, yield 50 %. Its solubility resembles that of the *ortho* isomer. (Found: Br, 24·6. $C_{13}H_8O_4NBr$ requires Br, 24·8 per cent).

The acid obtained by hydrolysis was identified as *m*-bromobenzoic acid (mixed m. p.). The nitrophenol being soluble in water, the solution was evaporated to dryness and the residue extracted with ether. It was found to be *m*-nitrophenol (mixed m. p.).

p-*Nitrophenyl* m-*bromobenzoate* was prepared in the same way as above. The solid obtained crystallises from acetic acid in white needles, m. p. 122°, yield 50 %. Its solubility resembles that of its other isomers. (Found: Br, 24·7. $C_{13}H_8O_4NBr$ requires Br, 24·8 per cent). The products of hydrolysis were identified as *m*-bromobenzoic and *p*-nitrophenol (mixed m. p.).

o-*Nitro-phenyl* 2:5-*dibromobenzoate*—To a mixture of *o*-nitrophenyl benzoate (12 g.) and bromine (16 g.) fuming nitric acid (*d* 1·45, 20 c. c.) was gradually added and the mixture was heated with a reflux condenser for about 12 hours. After dilution and neutralisation with sodium carbonate, a pasty mass was obtained, which solidified in the refrigerator. It crystallises from acetic acid in white

needles, m. p. 132°, yield 40 %. It resembles the monobromo derivative in solubility. (Found : Br, 39·6. $C_{13}H_7O_4NBr_2$ requires Br, 39·9 per cent).

The products of hydrolysis were identified as 2:5 dibromobenzoic acid (Claus and Reh, *Annalen*, 1891, **266**, 207) and *o*-nitrophenol (mixed m. p.).

m-*Nitrophenyl* 2:5-*dibromobenzoate* was prepared in the same way as the *ortho* isomer by heating the mixture for 8 hours, yield 60%. It crystallises from glacial acetic acid in white needles, m. p. 165°. It resembles the *ortho* isomer in solubility. (Found : Br, 39·8. $C_{13}H_7O_4NBr_2$ requires Br, 39·9 per cent)

This compound can also be prepared by brominating *m*-nitrophenyl *m*-bromobenzoate in presence of fuming nitric acid, but the yield is poor.

The products of hydrolysis were identified as 2:5-dibromobenzoic acid and *m*-nitrophenol (mixed m. p.).

p-*Nitrophenyl* 2:5-*dibromobenzoate*.—To a mixture of *p*-nitrophenyl *m*-bromobenzoate (8 g.) and bromine (4·5 g.), fuming nitric acid (*d* 1·45, 12 c. c.) was gradually added, and the mixture heated with a reflux condenser on a water bath for 7 hours. The solid, obtained by treating the reaction mixture in the usual way, crystallises from acetone in bright needles, m. p. 183-84°, yield 35 per cent. It is sparingly soluble in acetone, chloroform and in alcohol, benzene and acetic acid. (Found : Br, 39·6. $C_{13}H_7O_4NBr_2$ requires Br, 39·9 per cent). This substance cannot be obtained directly from the original ester.

The products of hydrolysis were identified as 2:5-dibromo-benzoic acid and *p*-nitrophenol (mixed m. p).

Our thanks are due to Dr. T. S. Wheeler for the keen interest he has taken in this work.

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On the Fluorination of Organic Compounds. Part I.

By Prafulla Chandra Ray, Harish Chandra Goswami and Anil Chandra Ray.

Preparations of organic fluoro-compounds by following the usual methods of halogenation are beset with difficulties.

(*i*) *Direct substitution of hydrogen by flourine* is not advantageous as the reacting element is not easily obtainable and all organic substances are vigorously acted upon by fluorine, which brings about a complete disruption of the molecule with the liberation of hydrofluoric acid and charring.

(*ii*) *Addition of hydrofluoric acid to unsaturated bodies* has equally led to negative results as hydrofluoric acid never adds up to unsaturated linkings. This property of hydrofluoric acid is in accordance with the properties of the halogen hydrides, the reactivity of the hydrogen fluoride being much less than that of hydrochloric acid.

(*iii*) *Substitution of the hydroxyl group by flourine* has also been attempted. Direct esterification of alcohol by hydrofluoric acid even in a concentrated solution is not advantageous as was shown by Sidney, Young and Meslans (*Compt. rend.*, 1892, **115**, 1080).

The technical difficulties in the employment of hydrofluoric acid, the impossibility of using glass apparatus and consequent necessity of using platinum vessels have generally discouraged the investigations with hydrofluoric acid.

To minimise the difficulties metallic fluorides have often been employed. Thus Moissan (*Bull. Soc. Chim.*, 1891, *iii*, **5**, 456) introduced silver fluoride as the fluorinating agent. Meslans (*Compt. rend.*, 1892, **114**, 1020) obtained acetyl fluoride by the action of anhydrous zinc fluoride on acetyl chloride. Swarts (*Bull. Soc. Chim. Belg.*, 1930, **39**, 444) introduced SbF_5 (with $SbCl_5$ or bromine as catalyst) as well as H_2F_2 as fluorinating agents.

In a recent communication on the ethyl and methyl esters of fluocarbonic acid Sarkar and Goswami (*J. Indian Chem. Soc.*, 1933, **10**, 537) have employed anhydrous thallous fluoride as the fluorinating agent. They have prepared methyl and ethyl esters of fluocarbonic acid by the action of anhydrous thallous fluoride on the methyl and ethyl esters of chlorocarbonic acid.

In continuation of their work we tried to prepare some new organic fluo derivatives and the present communication describes this attempt.

We have prepared monofluoacetone, ω-fluoacetophenone and fluoacetal by the action of anhydrous thallous fluoride on the corresponding bromo derivatives. The boiling point, density and refractive index of the fluo derivatives are given below.

	B. p.	Density.	Ref. Index.
Fluoacetone	72·5°	d24°, 0·967	1·3693 (21°)
Fluoacetophenone	98°/8 mm.	d33°, 1·154	1·5301 (28·9°)
Fluoacetal	60°/125 mm.	d340°, 1·447	1·4363 (34°)

Experimental.

Fluoacetone.—Bromoacetone (27 g.) was refluxed at 85-95° for 45 hours with powdered anhydrous thallous fluoride (48 g.) mixed with 25 c. c. of dry ether. The upper part of the condenser was fitted with a calcium chloride guard tube. When the reaction was over the product was filtered in a suction pump and the filtrate distilled. It was purified by redistillation (b.p. 72·5°), yield 10 g. (66%). It is a pungent smelling light yellow liquid, slightly soluble in water. (Found: C, 47·01; H, 6·63; F, 24·61. $C_3H_5O_2F$ requires C, 47·3; H, 6·5; F, 25·0 per cent).

Fluoacetone semicarbazone.—Fluoacetone (5 g.) was added to a saturated solution of semicarbazide hydrochloride and to this excess of a saturated solution of sodium acetate added. The semicarbazone precipitated out on stirring with a glass rod. It was filtered off, washed with a little water, dried and analysed, m. p. 131·5° (decomp.). It is a white crystalline solid slightly soluble in water. (Found: N, 31·05; F, 14·1. $C_4H_8ON_3F$ requires N, 31·4; F, 14·28 per cent).

Fluoacetophenone.—Bromoacetophenone (20 g.) was refluxed for 45 hours with anhydrous thallous fluoride (23 g.) in 40 c. c. absolute alcohol. The product was then filtered and the filtrate after removing the alcohol on a water-bath, was then distilled at 98°/18 mm., yield 11 g. (79 %). It is a brown pungent smelling, lachrymatory liquid. It forms additive compounds with pyridine and quinoline. (Fouud: C, 69·35; H, 5·42; F, 13·5. C_8H_7OF requires C, 69·56; H, 5·07; F, 13·75 per cent).

Pyridine addition compound.—Pyridine and fluoacetophenone in equimolecular proportion are dissolved in ether and mixed together. The mixture was slightly warmed when a turbidity appeared. After 48 hours the additive compound precipitated out. It was filtered, washed with ether and recrystallised from alcohol. It formed white needles, soluble in water, m. p. 161°. (Found: N, 6·04. $C_{13}H_{12}ONF$ requires N, 6·4 per cent).

Quinoline addition compound.—Ethereal solutions of equimolecular quantity of quinoline and fluoacetophenone were mixed together and warmed on a water-bath. After 12 hours the additive compound precipitated out and was recrystallised from alcohol as white needles by the addition of ether. It is soluble in water. It becomes brown at 231°. (Found: N, 5·1. $C_{17}H_{16}ONF$ requires N, 5·2 per cent).

Fluoacetal.—Bromoacetal (60 g) was mixed with powdered anhydrous thallous flouride (70 g.) and the mixture refluxed on an electric heater for 24 hours The condenser was provided with a calcium chloride guard tube. When the reaction was over the solution was filtered off and the filtrate distilled at 60°/25 mm. was collected, yield 22 g. (55%). It is a light yellow liquid with a pungent smell. (Found: C, 52·51; H, 9·7; F, 13·7. $C_6H_{13}O_2F$ requires C, 52·9; H, 9·5; F, 13·97 per cent).

Method of Analysis

Estimation of C *and* H.—The analysis was carried out as recommended by Moissan (*Ann. chim. Phys.*, 1890, *vi*, **19**, 277). The combustion was effected in a current of oxygen in a metal tube of copper by means of a mixture of CuO (80%) and litharge (20%), the latter retaining all fluorine as oxyfluoride.

Estimation of fluorine.—Fluorine was estimated by the method of Chablay modified by Vaughan and Nieuwland (*Ind. Eng. Chem. Anal. Ed.*, 1931, **3**, 274) and later on by Govaert (*Compt. rend.*, 1932, **195**, 797).

Estimation of N.—This was done by H. Ter Meulen's method, but the nitrogen in the semicarbazones was estimated by Duma's method.

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Chemical Aspects of Biological Oxidations.*

By Nil Ratan Dhar, D.Sc. Dr.es.Sc., F.I.C., I.E.S.

In my last address to the Society, I pointed out that the most fundamental processes taking place on the surface of the earth depend on the following reversible reaction,

$$6CO_2 + 6H_2O + E \rightleftharpoons C_6H_{12}O_6 + 6O_2.$$

One side of the above reaction was discussed last year and in this address I shall consider some aspects of the chemistry of respiration.

Introduction.

The scientific study of life phenomenon was initiated by Lavoisier when he declared in 1780 that *life is a chemical process* ("La vie est une fonction chimique"). This savant clearly recognised from his experiments that life processes are those of oxidation resulting in the liberation of heat. With a clarity of vision, which is the unique characteristic of this investigator, he established that the quantity of oxygen absorbed and of carbon dioxide excreted depends principally on (1) food, (2) work, and (3) temperature, within a few years of his discovery that oxygen supported combustion. Writing in 1849, Regnault and Reiset stated that modern researches have amply confirmed these far-reaching conclusions of the illustrious savant. ("Les recherches modernes ont confirme ces vues profondes de l' illustre savant."). Oxidation is the central life process sustaining the complicated machinery of the living.

The substances undergoing oxidation in the animal body comprising of carbohydrates, fats and proteins are not oxidised readily under ordinary conditions outside the body, although in the animal and plant tissues they are burnt up with ease into their end products.

* Presidential Address delivered at the Eleventh Annual General Meeting of the Indian Chemical Society, held in January 4, 1935 in Calcutta.

The problem of the mechanism by which animals and plants can accomplish the oxidation of the food materials so readily has occupied the attention of scientists since the days of Lavoisier. It is generally believed that oxygen must in some way be activated in the living tissues.

Induced Oxidation of Carbohydrates, Fats, Proteins, etc., and the Induced Oxidation Theory of Biological Oxidations.

Some interesting observations made in the author's laboratory seem to point to far-reaching conclusions with regard to the metabolism of carbohydrates, fats and proteins in normal healthy animals and plants.

In several publications from this laboratory, it has been shown that substances like glucose, starch, cane sugar, glycogen, butter, egg-white, egg-yellow, tartrates, citrates and fatty acids like palmitic and stearic acids, and numerous other substances, which are not directly oxidised by atmospheric oxygen at ordinary temperatures, can be oxidised by simply passing air through their solutions or suspensions, when they are mixed with compounds like sodium sulphite or freshly precipitated ferrous, cerous, manganous and other hydroxides, all of which undergo oxidation readily. It is important to note that in each case, the substance is oxidised to carbon dioxide and water, without the formation of any intermediate compound. A molecule of acetic acid containing two carbon atoms, and a molecule of stearic acid which contains eighteen carbon atoms, are equally well oxidised to carbon dioxide and water; the same is the case with alcohol containing two carbon atoms and glucose containing six carbon atoms.

One cannot but be struck by the close analogy between these slow and induced oxidations and biological oxidations in a normal individual or a plant. The normal metabolism of carbohydrates and fats gives rise to carbon dioxide and water only and to no intermediate products. Such products as glycuronic acid from glucose and diacetic acid from fatty acids, make their appearance only in their abnormal metabolism, as in intoxication with phenol, chloral, etc., or in diabetes or in fasting or as a result of continued vomiting or in poisoning with drugs like phlorhizin, etc. It is also interesting to note that exactly similar intermediate products are obtained in the case of rapid oxidation with hydrogen peroxide and a ferrous or ferric

salt (Dakin, Kostychev, Jolles, Dhar and Chakravarti). But the products of slow and induced oxidation of carbohydrates and fats are exactly identical with those of the normal metabolism of these substances in the animal body or plant tissue.

The behaviour of some of the polybasic acids is also instructive. Oxalic acid, the simplest member of the group is very rapidly oxidised by many laboratory reagents, but is oxidised with great difficulty in the animal body. Malonic, succinic, glutaric, tartaric and citric acids, however, are readily oxidised in the body, although they are more stable than oxalic acid towards many oxidising agents. It will be of interest to note that oxalic acid and oxalates are oxidised with very great difficulty by induction *in vitro* whilst tartaric acid and tartrates and citric acid and citrates can be readily oxidised by induction.

A systematic investigation of induced oxidations of the above type has been carried out in the author's laboratory. Suffice it to say here that oxidation of a wide variety of compounds has been effected by atmospheric oxygen in the presence of inductors like insulin, glutathione, sodium sulphite, colloidal phosphorous, freshly precipitated ferrous, cerous, manganous, uranous and other hydroxides at ordinary temperature (20-30°). Our recent experiments show that in presence of traces of copper compounds the induced oxidation of glucose, tartrate, etc., is markedly facilitated. Hence it appears that in the treatment of metabolism diseases or anæmia, the addition of traces of copper salts to iron or manganese preparations may be useful. It is highly significant that many of these substances yield carbon dioxide and water, products of normal metabolism. Knowing what one does of the products, which are formed by the action of other oxidising agents, one cannot but be impressed by the parallelism, which this suggests. Not only the products of induced oxidation are carbon dioxide and water but the oxidation of these substances to carbon dioxide and water is quantitative. It seems probable, therefore, from the analogy of these experiments *in vitro*, that biological oxidations can be classed under induced reactions; and that there exists in the animal body and plant tissues readily oxidisable substances, the oxidation of which induces the oxidation of food materials. Moreover, most of the vitamins, which are absolutely necessary for healthy life have been found to be good reducing agents capable of taking up oxygen directly from air and thus help the induced oxidation of food materials with which they are associated.

Comparative Experiments on the Oxidation of Proteins, Carbohydrates and Fats.

Inductor—cerous hydroxide. 60 Litres of air passed in 9 hours.

Substance.	Amount of substance oxidised.
Egg-white	83·3%
Egg yellow	69·4
Starch	57·2
Glucose	36·5
Butter	29·9

These substances fall in the following order according to their ease of oxidation. Egg-white > egg-yellow > starch > glucose > butter. In other words, proteins are more readily burnt than carbohydrates, which in their turn, are oxidised with greater ease than fat The order is the same as that given by Voit, who stated that "the metabolism in the body is not proportional to the combustibility of the substances outside the body; but protein which burns with difficulty outside, metabolises with the greatest ease than carbohydrates, while fat which readily burns outside is the most difficultly combustible in the body." This conclusion was arrived at by Voit from actual feeding experiments. These results show with what great success, biological oxidations have been imitated outside the body. The foregoing results can throw light on the problem of protein metabolism in the animal body. It is well known that the increase in metabolism is greater in the case of protein than with any other food-stuff. This increased metabolism called the *specific dynamic* action of protein by Rubner, has not been satisfactorily explained by physiologists. According to our results the protein is more readily oxidised than carbohydrates and fats and it is expected that in the animal body protein is more readily burnt than carbohydrates and fats and that is why more heat is generated in an unit time than with carbohydrates and fats. The recent experiments of Atma Ram and Dhar show that under comparable conditions the amino acids like α-alanine and aspartic acid are oxidised to a greater extent than cane sugar, glucose, sodium palmitate, stearate, oleate, etc., when exposed to air and light *in vitro*.

Recent Evidence in favour of the Induced Oxidation Theory.

Within recent years some evidence has accumulated in favour of this theory of biological oxidations, because most of the biologically active compounds like insulin, ascorbic acid (vitamin C), carotene (pro-vitamin A), lactoflavin (vitamin B_2), "ovoflavin," the oxidation ferments of Warburg, etc., have been found to be excellent reducing agents, capable of taking up oxygen directly from air. The energy obtained from these oxidations seems to initiate the oxidation of the food materials. Some important work on yellow oxidation enzymes has been published by Warburg and Christian (1932-33). The yellow enzyme is believed to contain a colloidal carrier and a pigment which on irradiation in alkaline solution produces the substance $C_{13}H_{12}O_2N_4$ (m.p. 320°). The *leuco*-form of the enzyme in presence of atmospheric oxygen produces the yellow enzyme and H_2O_2. With methylene blue the yellow enzyme and *leuco*-methylene blue are produced. Since the enzyme contains no metal, its oxygen transport is not inhibited by CO or HCN. It is believed by Warburg that this yellow enzyme causes the oxygen transport in anærobic lactic acid cultures and is present in all cells including those of higher animals. On the other hand, Keilin (1933) has concluded from spectroscopic investigation of some bacteria that the shading in the yellow (5900Å) and the band in the red (6300Å) are not the absorption bands of the oxygen transporting enzyme as believed by Warburg but are those of derivatives of cytochrome and probably of its component—a.

Moreover, recent research has shown that vitamin C seems to be identical with ascorbic acid, which is a marked reducing agent capable of inducing the oxidation of food materials. It is believed that vitamin C, whilst retaining most of its activity may be reversibly oxidised and the labile structure of ascorbic acid fits it well for such function. According to Müller (1933) and others the reducing property of aqueous humour of cattle and rabbit is also due to vitamin C. Ascorbic acid can be oxidised reversibly and irreversibly and it is to the double function of oxidation and reduction in the reversible change that the acid probably owes its biological activity. The parallelism between the reducing power and the antiscorbutic potency of plant extracts has been investigated by several workers. Tillmans, Hirsch and Jackisch (1932) have reported that the vitamin C content and the reducing capacity are, under many conditions, strictly parallel. Moreover, the reducing substance studied by them may be oxidised, like hexuronic acid, in a reversible and irreversible manner.

Similarly Peters and collaborators (1929-33) have shown that the brains of polyneuritic pigeons have a high lactic acid content and the brain tissue from such pigeons has a sub-normal oxygen intake and that on adding a concentrate of vitamin B_1 to the tissue, the oxygen intake is enhanced.

Recently a number of naturally occurring colouring matters, which are water soluble nitrogenous dyes, have been obtained from different sources. These dyes called flavins or lyochromes have been isolated from animal liver and kidney and from egg-white and milk whey. These dyes are believed to be related to the oxidation ferments prepared by Warburg and Christian (1932). The dye obtained from egg-white is termed "ovoflavin" and is reduced and decolourised by reducing agents and regains its colour when shaken in air. The change flavin $\rightleftharpoons$ *leuco*flavin is believed to depend on the transference of oxygen. The crystalline orange-brown dye from whey named "lactoflavin" has the composition $C_{17}H_{20}O_6N_4$ and resembles "ovoflavin" closely in composition and absorption spectrum. Both of these flavins are not only related to vitamin B_2, but lactoflavin is believed by Kuhn and his colleagues (1933) to be identical with vitamin B_2. During the last few years important researches on natural polyene pigments (lyochromes) have been published by P. Karrer and R. Kuhn and their collaborators. These pigments are widely distributed in the vegetable and animal kingdoms and comprise hydrocarbons, alcohols, xanthophylls, phytoxanthins, ketones, carboxylic acids and carboxylic esters. Carotene contains three distinct substances, two of which α-and β-carotenes, contain 11 double bonds and like vitamin A promote growth of animals. β Carotene is more allied to vitamin A biologically and chemically and Kuhn and collaborators have advanced the view that one mole of β-carotene can form two moles of vitamin A in the animal body as represented in the following equation,

$$C_{40}H_{56} + 2H_2O = 2C_{20}H_{30}O.$$

It is believed that kryptoxanthin, is also a pro-vitamin A like α-, β-and γ-carotenes.

Glutathione and Internal Secretion as Inductors of Biological Oxidations.

It is interesting to note that experiments carried on in the author's laboratory have shown that insulin and glutathione can act as inductors

in the oxidation of glucose solutions at ordinary temperature by simply passing air. Hopkins (1921), Harrison (19 4), Dixon (1929), Meldrum (1930) and others were successful in oxidising amino acids, proteins and fats by air in presence of glutathione. They were, however, unable to oxidise carbohydrates in the same manner. We have observed that in presence of small amounts of cerous, ferrous, manganese or cupric hydroxide either occuring singly or in mixtures of two or three, the addition of glutathione markedly increases the oxidation of glucose.

In this connection, it will be of interest to note that Oparin (1921) has stated that a dipepside, chlorogenic acid $C_{32}H_{38}O_{11}$ occurs in over a hundred different plants and it is readily oxidized in air losing four hydrogen atoms and forming a green product. It is believed that chlorogenic acid is more particularly active in the oxidation of amino acids, peptides and peptones forming ammonia, carbon dioxide and aldehyde. The author is of opinion that the oxidation of chlorogenic acid by air induces the oxidation of food materials, especially of proteins.

Moreover, glutathione is of common occurrence in animal and plant tissues. The colour by which glutathione is recognised is less intense in vegetable than in animal tissues. The oxidation of glutathione by air is likely to induce the oxidation of food materials in the vegetable and animal tissues as it does *in vitro*. As the amount of glutathione appears to be less in vegetable tissues than in the animal ones, the intensity of oxidation in the animal cells is greater than in plant cells. This is perhaps one of the factors which lead to a less active metabolism in plants than in animals.

Holmes (1926) has found that in general the tumour cells contain abnormally small amounts of reduced glutathione and may be slow in reducing the dipeptide added in the oxidised form. Rat sarcoma and carcinoma tissues were found to be deficient in the respiratory pigment cytochrome. Crabtree (1929) has shown that the glycolytic activity of tumours exerts a checking effect on their respiration. Very recently Heinlein (1932) has reported that the glutathione content of tumours (Ehrlich mouse carcinoma, Rous sarcoma and human carcinoma) is lower than that of normal organs. If this contention of Holmes and Heinlein that cancerous tissues contain abnormally small quantities of reduced glutathione and the respiratory pigment cytochrome is correct, it appears that the oxidations of glucose and lactic acid are less in such tissues because the inductors glutathione and

cytochrome exist in smaller amounts in cancerous than in normal tissues. These observations of Holmes and Heinlein lend support to the author's view that biological oxidations are really cases of induced oxidations.

It will be interesting to note that the glutathione content of muscles in which oxidation processes are supposed to take place at an intense rate is small as will be evident from the following values.

Tissues.	Fed animal (dog).	Tissues.	Fed animal (dog).
Liver	0·21	Spleen	0·09
Lungs	0·08	Heart	0·08
Muscle	0·05	Testicle	0·06
Kidney	0·14	Brain	0·06
		Adrenaline	0·00

It is well known that roughly two-thirds of the body energy necessary for animal life are obtained from the slow combustion of glucose and as the glutathione content in muscles is small, it can be concluded that glutathione is not the chief catalyst or inductor in carbohydrate oxidation in the body.

F. G. Benedict (1932) has come to the conclusion that the relatively low heat production with cold blooded animals in comparison with the warm blooded animals of the same size is due to the difference in the distribution of the blood carrying the three important factors of metabolism, *viz.*, oxygen, nutrients and hormones and that increased blood flow is associated with increased metabolism. In the cold blooded animals, the amount of blood is relatively less than in warm blooded animals. The heat production in the body seems to be controlled by the blood supplied to the tissues. Where there is a liberal blood supply to the tissues, the heat generation can be high, where the blood supply is low, the heat production must be low also. The blood distribution is not determined by the metabolism, because with man the same blood distribution may permit his metabolism to be increased 1000 % in extreme cases. Lusk (1919) has stated that in starvation, amongst the various body organs, the greatest loss in weight is suffered by the glands and that their activity is greatly reduced.

Hence it seems likely that the internal secretions possibly acting as inductors, largely control animal oxidation. In starvation, the

amount of internal secretion available for accelerating the oxidation decreases and hence the metabolism is decreased. In violent exercise, the metabolism is highly increased probably due to the increase in the oxygen intake and a greater supply of internal secretions from the various glands. It appears that although glutathione and other reducing agents present in the blood are of some importance in animal metabolism, the chief inductor seems to be the internal secretions.

Respiratory Pigments and Plant Respiration.

Palladin (1908) has reported that when plant tissues are extracted with boiling water, a colourless chormogen is obtained and these chromogens called by Palladin as "respiratory chromogens" are believed to be widely distributed in the plant kingdom. It will be of interest to note that Palladin assumes with others that the atmospheric oxygen oxidises only the hydrogen of the respiratory chromogens and this reaction is aided by the peroxidases and is not concerned with the oxidation of the carbon of the food materials.

Haas and Hill (1925, 1926) have extracted a colourless chromogen from the leaves of *Mercurialis perennis*. This chromogen named hermidon by Haas and Hill has a marked affinity for oxygen. It has been suggested by Haas and Hill that hermidon takes part in the respiration of *Mercurialis perennis* and when the respiration of the plant is high in summer and spring, the amount of hermidon in the leaves is abundant.

A blue pigment has been observed by Roach (1925) in slightly sprouted potatoes placed over-night in a vacuum dessicator in an atmosphere of carbon dioxide and then powdered. When air is allowed to enter, the blue colour becomes more marked and finally, a light yellow colour is obtained. It appears that potatoes contain a compound like hermidon.

The isolation of chlorogenic acid by Oparin and its probable usefulness in plant respiration has already been pointed out.

Different authors have advanced different views on plant respiration but there is not much agreement in these views. The hypothesis of Palladin has already been discussed. Professor Blackman of Cambridge (1928) from his experiments with Parija on the respiration of ripening apples has postulated that there are at least four stages in the process of respiration, *viz.*,

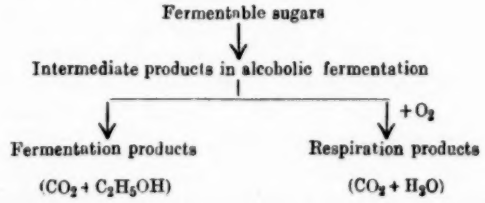
(*i*) The hydrolysis of the carbohydrate to hexoses.

(*ii*) The hexoses pass to an activated form.

(*iii*) The activated hexose undergoes glycolysis with the formation of lactic and pyruvic acids, acetaldehyde, etc.

(*iv*) In presence of oxygen, these products of glycolysis undergo oxidation to carbon dioxide and water. In absence of oxygen, *i.e.*, in anærobic conditions, alcohol and carbon dioxide seem to be produced. According to Blackman, the velocity of glycolysis is the slowest of the various stages and thus controls the velocity of the respiration.

On the other hand, Kostychev is of opinion that alcoholic fermentation and sugar respiration are connected phenomena and he represents the two phenomena as follows:—



According to Kostychev, there are two steps in the process of normal respiration in plants *viz.*, (*i*) the anærobic cleavage, and (*ii*) their subsequent oxidation. In other words, Kostychev is of opinion that the first stage of oxygen respiration is anærobic respiration and anærobic and oxygen respirations are connected. In this connection, it will be of interest to note, that parasitic worms (*ascaris*), earth worm (*lumbricus*) *infusoria*, leech, etc., produced carbon dioxide and sometimes fatty acids as well when deprived of oxygen and hence anærobic life of lower organisms is also possible. On the other hand, experiments in the absence of oxygen cannot proceed far with warm blooded animals without causing death, because the tissues and especially, the nervous tissues appear to be extremely sensitive to absence of oxygen.

The views of Blackmann and Kostychev rest on the assumption that glucose is the only material available for plant respiration. But it is a well established fact that proteins and fats are also used up in plant respiration. Hence, it appears that so far no comprehensive theory of plant respiration, embracing the metabolism of the three chief varieties of food materials, carbohydrates, fats and proteins, has been advanced. It seems to the author that the mechanism involved in the oxidation of food materials in the plant is the same as in the animal metabolism, and the phenomenon of induced oxidation of food materials in the

presence of easily oxidisable substances like glutathione, chlorogenic acid, Palladin's "respiratory chromogens", Keilin's cytochrome, insulin, etc. form the basis of plant and animal respiration. It is well known that the conversion of glucose into alcohol and CO_2 and the oxidation of glucose to CO_2 and water are exothermal chemical changes. The formation of alcohol from glucose according to the equation,

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

is a typical case of an auto-oxidation and reduction process well known in chemistry such as the following decompositions:

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

$$2H_3PO_2 = H_3PO_4 + PH_3 \ ;$$

the well known Cannizzaro reactions are also exactly similar. These auto-oxidation and reduction processes are less exothermic than the reactions involved in the complete oxidation of the reducing substances. Thus for the same amount of glucose the heat generated is greater when it is oxidised to CO_2 and water than in its conversion into alcohol and CO_2. That there is a greater possibility of the occurrence of an auto-oxidation and reduction reaction than a reaction involving complete oxidation is due to the fact that the energy difference in the original reacting substances and the products formed is greater in the reactions involving complete oxidation than in the auto-oxidation reduction processes.

The plant physiologists like Kostychev, Blackmann, Palladin and others being familiar with anærobic respiration have based their views regarding the mechanism of plant respiration on the similarity of the processes involved in ærobic and anærobic respirations. In the fermentation of glucose forming alcohol and CO_2 several enzymes are believed to take part and some of these enzymes have also been detected in plants, *e.g.* hexosephosphatase in peameal, ketonaldehyde mutase, carboxylase, etc. Moreover, several co-enzymes which activate the enzymes have also been found in some plants. The enzymes aided by the co-enzymes can behave as typical catalysts in accelerating the exothermal reaction,

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

In other words, as far as anærobic respiration is concerned the theories of Palladin, Kostychev and Blackman have a large amount of experimental evidence in their support. On the other hand, the schemes of these plant physiologists seem unsatisfactory when we consider ærobic respiration, which is certainly of greater importance in normal plant life than anærobic respiration. It is well known that ordinary oxidising enzymes are unable to oxidise even small amounts of glucose in presence of air. What is the mechanism by which the labile intermediate products formed from hexose by the action of zymase in the scheme of Kostychev are oxidised to CO_2 and water in presence of air ? In Blackman's scheme, in the process of glycolysis caused by the group of enzymes present in zymase, a number of intermediate compounds, *e.g.* methylglyoxal, lactic acid, pyruvic acid and acetaldehyde are supposed to be formed. Moreover, in the Embden-Meyerhof scheme (1933) recently advanced, the intermediate formation of pyruvic acid, acetaldehyde, etc , has been assumed. Now most of these compounds which are supposed to be formed as intermediate products in fermentation and in respiration are incapable of taking up oxygen directly from the air and undergo oxidation to CO_2 and water, which are the final products of respiration in the animals and plants under normal conditions.

On the other hand, not only these substances but all food materials are finally oxidised to CO_2 and water in the animal and plant tissues in presence of air. Consequently the theories of Palladin, Kostychev and Blackman do not explain the final process in ærobic respiration.

Agencies helping Biological Oxidations.

It seems to the author that the following agencies are effective in bringing about the oxidation of food materials not only in animal life but also in plant respiration.

(1) Reducing agents like glutathione, chlorogenic acid, ascorbic acid, Palladin's "respiratory chromogens," Keilin's cytochrome, ovoflavin, lactoflavin, internal secretions, etc. These substances take up oxygen directly from the air and induce the oxidation of food materials.

(2) The surface of the plant and animal cells.

(3) The presence of small quantities of iron and possibly traces of manganese and copper compounds.

(4) Mild alkalis and phosphates.

(5) Sunlight.

All these agencies seem to have their relative importance in causing the oxidation of the food materials possible in the plant and animal tissues, although they are not oxidised in the air outside. There is reason to believe that in animal oxidation the internal secretions play an important rôle. It is well known that Nature hardly depends on one agency in carrying on its mechanism and in bringing about the oxidation of glucose and other oxidisable materials, seems to take recourse to the foregoing agencies, which have been shown to accelerate the oxidation of food materials by air.

The induced oxidation theory of the mechanism of biological oxidations has more experimental evidence in its support than the surface oxidation theory of Warburg and the dehydrogenation theory of Wieland. Meyerhof failed to oxidise glucose by air on a charcoal surface and the theory of Wieland is not helpful in understanding the mechanism of the oxidation of glucose. (*cf.* Dhar, " New Conceptions in Biochemistry", 1932, pp. 18-20).

Are the "Acetone Bodies" Products of Normal Metabolism?

Many physiologists believe that β-hydroxybutyric acid, acetoacetic acid and acetone are intermediate products of normal metabolism, that the diabetic cannot further oxidise them, and that as such they are excreted in the urine.

It is established beyond doubt that the excretion of acetone bodies in the urine occurs only in conditions in which carbohydrates are either not being utilised owing to metabolic deficiency or is missing from the food. To the former category belong diseases like diabetes or cases of poisoning with drugs like phlorhizin ; to the latter, cases of continued vomiting or voluntary abstention from carbohydrate food. When acetonuria has made itself manifest as a result of lack of carbohydrates in the food, the administration of such food materials, causes the prompt disappearance of acetonuria or ketosis. It appears that for the complete combustion of fats, carbohydrates must be metabolised at the same time.

Various explanations have been suggested for the anti-ketogenic effect of carbohydrates. Geelmuyden (1904) has assumed a combination of acetone bodies and carbohydrates to occur before the oxidation of the former can take place. Woodyatt (1916) suggests that a coupled

reaction takes place between acetoacetic acid and glucose, glyceric aldehyde or some simple sugar, the sugar being oxidised and the acetoacetic acid being simultaneously reduced. Ringer (1914) assumes a combination of glucose and β-hydroxybutyric acid in order that the latter may be oxidised and Shaffer (1922) has arrived at the conclusion that two molecules of acetoacetic acid enter into reaction with one of glucose. There seems to be little experimental evidence in favour of these views on the anti-ketogenic properties of carbohydrates.

The author (1925) has advanced the following explanation based on experimental observations on the velocity of oxidation of carbohydrates, fats and proteins occurring singly or in mixtures: Under normal conditions, the heat and energy of the body are derived from the simultaneous combustion of carbohydrates, fats and proteins. When as a result of special conditions, carbohydrate is not oxidising more fat and protein must be burnt in order to maintain the body temperature and energy at its normal level. Hence in an unit time more fat would be burning than under normal conditions and combustion is likely to be incomplete, so that acetone bodies would be formed. It has been observed that whenever there is rapid combustion of fat, as for instance, in hyperthyroidism, there is the elimination of acetone bodies. The same is the case *in vitro* as well. Chakravarti and Dhar (1929) have observed that in the rapid oxidation of fatty acids by hydrogen peroxide and ferric salts, there is the formation of acetone bodies. They have also observed that if the rate of oxidation of fats be slowed down, as is the case when carbohydrates (*e.g.* glucose) are present, the amount of acetone bodies produced diminishes. Palit and Dhar (1930) have further observed that in the slow and induced oxidation of fats, acetone bodies are not formed at all, but only carbon dioxide and water, the products of normal metabolism.

It is evident, therefore, that acetone bodies are not products of normal metabolism, but result from abnormal conditions. The author has suggested that under normal conditions, fats are mainly burnt in the animal body directly to carbon dioxide and water, without the formation of intermediate products. An objection may be raised as to how a fatty acid molecule containing 18 carbon atoms can be directly oxidised to carbon dioxide and water without the formation of intermediate products. Many physiologists are of opinion that acetoacetic acid, with four carbon atoms in the molecule, undergoes complete oxidation to carbon dioxide and water without the formation of intermediate products. If a molecule with four carbon atoms can be directly

oxidised then the direct oxidation of more complex acids appears to be not impossible.

The hypothesis of the author that when fats are rapidly oxidised in the absence of carbohydrates and proteins intermediate toxic substances are produced, is supported by the observation of Pirschle (1926) that acetaldehyde is formed in the respiration of many fat-containing germinating seeds such as *Helianthus*, *Linum*, *Cannabis*, *Brassica*, *Raphanus* and *Cucurbita*. It is well known that the respiration of germinating seeds is very intense and hence when the fats in the germinating seeds are oxidised rapidly intermediate products such as aldehydes, etc., are formed and the oxidation of fats does not proceed to completion with the formation of carbon dioxide and water. It appears that the metabolism of fat in plants is allied to its metabolism in animals.

Oxidation effected by Hydrogen Peroxide differs from Biological Oxidations.

The supposed similarity between the oxidations taking place in the living body and those brought about by hydrogen peroxide *in vitro* (Dakin, Kostychev, and Jolles) is believed to lend strength to the peroxide theory of biological oxidations. Thus Dakin writes (1912) "An extraordinarily close similarity as regards the types of reactions exists between the two sets of phenomena. Thus normal saturated fatty acids in the body undergo oxidation in the β-position, butyric acid yielding acetoacetic acid, acetone and other products; hydrogen peroxide alone of all the various chemical oxidising agents brings about precisely the same reaction. Amino acids and ketonic acids, such as leucine and phenylpyruvic acids are oxidised to lower fatty acids with the liberation of carbon dioxide and either ammonia and water. Glucose may be oxidised in the body to glycuronic acid, while hydrogen peroxide is the only reagent capable of effecting this change outside the body. A great many other biochemical reactions of less strikingly characteristic type such as the oxidation of simple alcohols, aldehydes, etc., may be reproduced *in vitro* by means of hydrogen peroxide."

If we consider this statement, it will be at once clear that the similarity between the oxidations in the animal body and those *in vitro* effected by hydrogen peroxide is only sperficial. The intermediate products selected here for bringing the similarity into relief, namely glycuronic acid in the case of glucose, acetoacetic acid, acetone and other products in the case of butyric and other fatty acids, and carbon

dioxide and ammonia in the case of amino acids are not products of normal metabolism but are only obtained in certain pathological conditions. The end products of normal metabolism of glucose and fatty acids in a healthy individual are carbon dioxide and water. The introduction of camphor, chloral, etc., into a normal as well as diabetic person leads to the excretion of combined glycuronic acids.

Dakin (1908) has shown that ammonium butyrate on being oxidised with hydrogen peroxide and a ferrous salt, forms acetone, acetoacetic acid, acetaldehyde, etc. Chakravarti and Dhar have shown that volatile aldehydic or ketonic products are formed when carbohydrates, fats and nitrogenous substances are oxidised with hydrogen peroxide and a ferric salt at 37°. Hence *in vitro* when the food materials are rapidly oxidised, acetaldehyde and other intermediate products are obtained but when the oxidation of food materials is slow as in the cases of induced oxidation obtained by passing air, complete oxidation of food-stuffs takes place. In animals and plants, similar behaviour is also expected. The author has emphasised that in normal health the food materials taken in the body are completely oxidised into carbon dioxide and water without the formation of intermediate products, just as food materials are oxidised completely to carbon dioxide and water, when air is passed through their solutions or suspensions in presence of inductors or in sunlight. Intermediate compounds are only formed in the diseased condition of the animal body and plant tissues or when the nutrient material is oxidised quickly in the plants or animals.

It has been observed that volatile aldehydic or ketonic products along with carbonic acid are formed when carbohydrates, fats and nitrogenous substances are oxidised by hydrogen peroxide and an iron salt at 37°, whilst only carbon dioxide and water are obtained and there is complete oxidation when the above substances are oxidised by air in presence of ferrous hydroxide as inductor. It appears, therefore, that the intermediate iron peroxide obtained in the case of hydrogen peroxide and an iron compound must be different from that formed with the ferrous compound and oxygen, because the products of oxidation are different in the two cases.

Oxidation of Mixtures of Carbohydrates, Fats and Proteins.

Palit and Dhar (1928-1930) have carried on experiments on the induced oxidation of mixtures of carbohydrates, fats and proteins with

each other and have arrived at the important conclusion that the presence of any one of these substances, which is itself undergoing oxidation, retards the oxidation of the other.

Now in the normal health, the heat and energy of the body are supplied to the system from the simultaneous combustion of carbohydrates, fats and proteins. Our experimental results conclusively prove that the oxidation of fat is retarded by carbohydrates and perhaps less powerfully by proteins. It seems fairly certain now that the presence of either one or both of the above substances, which are undergoing oxidation, retards the oxidation of the third. It is, therefore, evident that in the presence of a large excess of carbohydrates and fats, little protein should burn. The protein-sparing qualities of carbohydrates and fats were discovered from feeding experiments by some of the earliest students of metabolism, and it is believed that carbohydrate is the more efficient of the two in sparing proteins. It has also been proved that the withdrawal of carbohydrates from the food increases the protein metabolism. Moreover, in diabetes, when the sugar passes out unoxidised, there is considerable waste of protein. The experimental results of Palit and Dhar provide for the first time a scientific explanation of these empirical observations of physiologists.

On the basis of the above results, a satisfactory explanation can be given on the onset of glycosuria, following the intake of phosphorus, arsenic, phlorhizin or other poisons. All these substances are marked reducing agents and therefere, in accordance with the general principle laid down in the opening paragraph of this section, they produce retardation of the oxidation of the glucose in the animal body. Hence some of the glucose escapes unoxidised in the urine and more protein should be metabolised in order to keep up the normal supply of the body heat and energy. In this connection it is interesting to note that phosphorus injections raise the protein metabolism of fasting dogs to 250, 260, 283, 248, 183 and 164 per cent of the normal. The percentage increase of protein metabolism in phlorhizin glycosuria is 540, 450 and 340. Moreover, it has been reported that administration of whisky favours the production of glucose in a diabetic. Apparently the easily oxidisable carbohydrates, which act as negative catalysts in the oxidation of fats, are necessary for the complete combustion of the latter.

If the acetone bodies are to be ascribed to the rapid but incomplete combustion of fats which is shown to take place in the diabetic,

it follows that, not only in diabetes but also in all other conditions, where there is rapid combustion of fats and little oxidation of carbohydrates, there should be acidosis and acetonuria. Indeed these conclusions are confirmed by experiments on human beings and animals carried out by several physiologists. Thus Bar (1905) has reported that a simple withdrawal of carbohydrates is followed in normal human beings accustomed to a mixed diet, and also in apes, by an acidosis, that is excretion of oxybutyric acid, acetoacetic acid and acetone with coincident increased elimination of ammonia. Deprivation of carbohydrate increases the body's need of fat and this flooding of the metabolic mill with fats results in their incomplete oxidation with the consequent production of acetone bodies. In starvation, or as a result of continued vomiting, acetonuria is observed after some days from the beginning of starvation, when most of the body store of glycogen has been utilised. In all such cases where acetonuria sets in as a result of simple carbohydrate deficiency in the food, the administration of carbohydrates causes the disappearance of ketosis. In hyperthyroidism too, where there is a rapid oxidation of fat, glycosuria and some times actual manifestations of diabetes have been observed.

If the oxidation of fats can somehow be retarded, then in diabetes there should be a marked decrease in the elimination of acetone bodies. Thus xylose, gluconic acid, citric acid, propionic acid, glutamic acid, glutaric acid, etc., have been found to decrease the formation of acetone bodies in diabetes. All the substances are utilised by the diabetic. Hence smaller amounts of fat need to be burnt. The author is of opinion that all these reducing substances, which are themselves oxidised in the body act as negative catalysts in the oxidation of fats, thus favouring the slow but complete oxidation of the latter with the resulting decrease of the acetone bodies.

Proteins also exert antiketogenic properties, although to an extent smaller than carbohydrates. Very little carbohydrate and a great deal of fat are taken by the Eskimos; but they eat an abnormally large amount of protein. In their case, the large amounts of proteins act like carbohydrates in retarding the oxidation of fats and thus assist their complete oxidation.

Use of Alkali Tartrates and Citrates in Diabetes and Fasting.

Our experimental results obtained in these laboratories, show that by the addition of sodium tartrate, the amount of potassium oleate

oxidised by induction in 30 hours by 73 litres of air is considerably decreased. In the case of ferrous hydroxide as inductor, in presence of sodium tartrate the percentage of potassium oleate oxidised in 7·9, whilst under identical conditions and in absence of sodium tartrate the percentage is 40·7. The corresponding results with cerous hydroxide as inductor are 16·8% and 45·1% respectively. Hence it is clear that the addition of a tartrate markedly decreases the velocity of the oxidation of potassium oleate. Moreover, the presence of oleate retards the velocity of the oxidation of sodium tartrate.

These results seem important from the point of view of the treatmentof diabetes and prolonged fasting. Under normal conditions the heat and energy of the body are derived from the simultaneous combustion of carbohydrates, fats and proteins. When as a result of special conditions such as diabetes, carbohydrate is not burning more fat and protein must be burnt in order to maintain the body temperature and activity at its normal level. Hence in unit time, more fat would be burning than under normal conditions, and the combusion of fat would be incomplete, so that acetone bodies would be formed. Chakravarti and Dhar (1929) have observed that in the rapid oxidation of fatty acids by hydrogen peroxide and ferric salts there is a formation of acetone bodies. They have also observed that if the rate of oxidation of fats be slowed down, as in the case when carbohydrates (*e.g.*, glucose), are present, the amout of acetone bodies formed diminishes. Palit and Dhar (1930) further find, that in the slow and induced oxidation of fat, acetone bodies are not formed at all, but only carbon dioxide and water, the products of normal metabolism.

Our experimental results show that just as carbohydrates decrease the velocity of oxidation of fats, similarly tartrates and citrates can also decrease the velocity of the oxidation of fats. Hence a tartrate or a citrate, apart from its power of acting as a buffer in removing the excess of hydrogen ion (H°) generated in the body, may serve as an antiketogenic substance like a carbohydrate. Thus the tartrates or citrates in drinks are likely to prove beneficial in the treatment of diabetes and long continued fasts, because in such cases the body has not lost the power of oxidation and is likely to utilise the tartrates and citrates as food along with the fats of the body.

In the plant kingdom, there are also examples of formation of intermediate substances in the process of respiration. Succulent plants

do not evolve carbon dioxide when placed in the dark, although oxygen absorption is active. In these cases organic acids like malic, oxalic etc., are formed and when the concentration of these acids becomes large, evolution of carbon dioxide as in normal plants takes place. It is assumed that this peculiar behaviour is associated with the massive structure of the succulent plants and fleshy fruits and the difficulty of the movement of the gases. It appears that in these plants, the supply of oxygen necessary for the complete oxidation of food materials to carbon dioxide and water is inadequate due to the slow movement of the gases. In some bacteria, acids are also formed in their oxidative activities.

The experiments of Stephenson and Whetham (1923) on the Timothy grass bacillus are of interest from the view point of the oxidation of a mixture of fats, proteins and carbohydrates in metabolism. The bacillus was cultivated at 37° on a medium containing ammonium phosphate as a source of nitrogen and glucose as the source of carbon. The p_H of the medium was 8·0. The sugar was used up in about three weeks but fats and proteins accumulated during this period. After three weeks, the amount of fats was burnt but the protein was not yet oxidised. There was no intermediate product of oxidation but carbon dioxide was given off. When the sugar was being oxidised, the respiratory quotient was high but later on in the process of fat combustion, the respiratory quotient became less. These results are easily explained from the view point that the complete oxidation of fat requires the presence of a negative catalyst which in this case is the protein, just as in the case of the food consumed by the Eskimos already referred to in which the large fat consumption is facilitated by the presence of considerable amounts of proteins. Another important point has been brought out by the investigations of Stephenson and Whetham. They studied the metabolism in slightly alkaline medium (p_H 8) and it has already been mentioned that Dhar and collaborators have observed that the oxidation of food materials is assisted by the presence of mild alkalis. It appears that the oxidation of fats and glucose in the experiments of Stephenson and Whetham was also facilitated by the alkaline medium.

Carbon-nitrogen Ratio in Natural Systems undergoing Oxidation.

It is well known that in soil, which is well-aerated, the chemical changes affecting the carbon and nitrogen present in the soil are

intimately connected. The combined nitrogen existing in the soil can form nitrate only if the ratio of C to N is smallar than 10. When the proportion of carbon is greater, the excess is oxidised to CO_2 and the nitrogen remains as complex protein. When, on the other hand, the proportion of nitrogen becomes greater than the above ratio, the nitrogenous compound is changed into ammonia and nitrate, which may be absorbed by the plant or lost from the soil by different agencies. The observations of Leighty and Shorey (1930), however, show that in the majority of soils examined by them the carbon-nitrogen ratio varied from 7 to 15 and in extreme case the ratio could be as small as 3 and as large as 35. It seems to the author that the soils examined by Leighty and Shorey were not properly aerated for a sufficiently long time. The constant r.tio is reached in soils which are sufficiently aerated. The value of the constant may vary with the climatic conditions because the relative velocity of the oxidation of carbonaceous compounds may not be the same at all temperatures.

The constancy of the carbon-nitrogen ratio in the soil has been ascribed to the activities of micro-organiams but it will be evident from the following considerations that the constancy of C to N is maintained even in the absence of bacteria in many natural systems undergoing oxidation in air and in the soil.

Dhar (1921) has observed that in the presence of sodium arsenite, which becomes oxidised when added to sodium sulphite exposed to air, the velocity of the oxidation of sodium sulphite by air is markedly retarded. Similarly, the presence of carbohydrates, which are themselves oxidised when mixed with a sulphite, ferrous hydroxide or cerous hydroxide, markedly diminishes the velocity of the oxidation of the last named substances. We have arrived at the generalisation that in oxidation reactions the phenomenon of negative catalysis is observed when the catalyst is a reducing agent. The experimental results obtained in these laboratories conclusively prove that the oxidation of fat is retarded by carbohydrates, and perhaps less powerfully by proteins. It is therefore, evident that in the presence of a large excess of carbohydrates or fats, little protein is burnt.

It will be interesting to note that in starvation the ratio of carbon to nitrogen metabolism (oxidation) is also not far from 10 as will be evident from the following results.

Animal ...	Dog.	Fowl.	Guinea pig.	Rabbit.
Ratio of C and N oxidised in starvation ...	9·5	10·8	7·6	9·7

If the starvation is continued further the value becomes less than 10 as will be seen in the following results obtained with a dog kept on starvation.

Days of starvation ...	4th-13th.	14th-15th.	16th-23rd.	24th-30th.	31st-35th.	3 ith.	37th.	38th.
Ratio of C and N oxidised in starvation ...	10·3	9·3	9·01	8·6	8·0	6·0	5·8	5·5

Following the lead of Doryland (1916) it has been assumed that the energy requirements of the bacteria present in the soil control the relative oxidation of the different groups of organic substances present therein. It is well known that the percentage of the energy utilised by the bacteria from an oxidation reaction is exceedingly small and thus it seems hardly probable that such inefficient processes should be able to regulate the various oxidation reactions taking place in the soil. The retarding influence of different carbohydrates and carbonaceous substances in the processes of ammonification and nitrification, is observed with different bacteria, fungi, etc., of different energy and food requirements, and is not regulated by their demands, but forms a part of a universal phenomenon taking place in the animal, plant and in soil and *in vitro* in which it is always observed that a readily oxidisable organic substance can act as a negative catalyst in the oxidation of another substance.

Are Organic Acids formed in Plant Respiration?

Mayer (1887) stated that in the plant respiration under certain conditions, oxalic and malic acids are formed and that sugars are produced from these acids in presence of light. The amount of malic acid in succulent plants increases at night and decreases in presence of light. It is of interest to note that Sir J. C. Bose (1924) has reported that *Hydrilla* can undergo marked photosynthesis in sunlight in the complete absence of carbonic acid but when fed with dilute solutions of malic or oxalic acid. In presence of sunlight, the organic acids can partially decompose into carbonic acid and are also oxidised to carbon dioxide and water, which undergo photosynthesis.

There is considerable difference of opinion regarding the origin of these organic acids detected in plant respiration. Some authors believe that sugars form organic acids whilst others ascribe them to proteins.

Sir J. C. Bose (1924) has observed that the *Hydrilla* plants become strongly acidic in summer (April), but the acidity disappears when the rainy season (July) sets in. It seems likely that in summer in the tropics, the temperature of the water in the ponds becomes high and the amount of dissolved oxygen which is necessary for plant respiration, becomes less. Hence the available oxygen essential for respiration decreases and the oxidation of the food materials present in the *Hydrilla* has to proceed in an insufficient supply of oxygen resulting in the production of organic acids, which are intermediate products of metabolism and not in the final products—carbon dioxide and water. There is another factor which may facilitate the formation of acids in the *Hydrilla* at the high temperature of the tropical summer. It has already been mentioned that the velocity of respiration is greater, the higer the temperature. Hence in summer months, the oxidation of food materials in the *Hydrilla* is rapid but it has already been emphasised that there is greater likelihood of the formation of intermediate products of metabolism and not of the final products—carbon-dioxide and water, when the metabolism of food materials is rapid than when it is slow. Hence at high temperatures, the *Hydrilla* forms acids by respiration. It is well known that the respiration of germinating seeds is very intense and that is why, we can expect the formation of intermediate products in the respiration of germinating seeds. Thus Pirschle (1926) reported the formation of acetaldehyde in the respiration of many carbohydrate, protein and fat-containing germinating seeds.

It appears, therefore, that organic acids, aldehydes and other intermediate products are formed in plants (specially in fleshy fruits and succulent plants) under special circumstances when the oxidation of food materials takes place very rapidly or in a limited supply of oxygen. In the animal body also, intermediate products are formed under similar conditions.

Photo-oxidation of Carbohydrates, Fats and Nitrogenous Substances by Air in Sunlight and Influence of Light on Respiration.

It has been shown by Dhar and Sanyal (1925) that methyl alcohol, ethyl alcohol and glycerol are oxidised by passing air at the ordinary temperature in the presence of sunlight.

Pa'it and Dhar (1928-1934) have made a systematic investigation of the oxidation of various substances by air in sunlight at the

ordinary temperature. They have shown that different carbohydrates, glycogen, urea, glycine, hippuric acid, α-alanine, sodium urate, potassium palmitate, stearate, oleate, sodium formate, tartrate, oxalate, lecithin, cholesterol, butter, milk, egg-white, egg-yolk, etc., can be oxidised photochemically by passing air.

Moreover, it has been shown that in the presence of zinc oxide, and ferric and uranium nitrates, which act as photo-sensitisers, the amount of oxidation of the foregoing substances is greatly accelerated.

All the above substances are completely oxidised to carbon dioxide and water without the formation of intermediate products. Hence light accelerates the oxidation reactions on which animal life depends. Palit and Dhar have also carried out comparative experiments on the oxidation of egg-white, egg-yolk, starch, butter, glucose, cane sugar, and glycogen in sunlight, and the following are the results, amount oxidised being given in parantheses: egg-yolk (60·9%) egg-white (31·25%), starch (8·2%), butter (31·8%), glucose (13·6%), cane-sugar (7·8%), glycogen (7·5%).

It appears, therefore, that egg-yolk is the most easily oxidisable substance in presence of light; then come starch and also butter, which are oxidised with greater ease than sugars, which are the least oxidised. These results on the oxidation of food materials by air in sunlight are suggestive, and the beneficial influence of light in the treatment of disease may be due to an increased metaboilism in light.

The following results obtained by Glitscher and Hasselbach (1926) show that light can actually penetrate through epidermis. The rays of shorter wave-length are absorbed by the thinnest layers of the epidermis. On the other hand, rays of longer wave-length can penetrate to appreciable depths.

Wave-length	Percentage transmission by epidermis	
	0·1 mm. thickness.	1 mm. thickness.
4360Å	59	0·5
4050	55	0·3
3660	49	0·08
3540	42	0·02
3130	30	0
3015	8	0
2990	2	0
2970	0·01	0

From their researches on the photo-oxidation of food materials by air in sunlight at the ordinary temperature, Palit and Dhar have concluded that the light absorbed by the system accelerates the metaboilism of food materials in the body. The person thus has a sense of well-being when exposed to light and disease is avoided. Sunlight is appreciably transmitted by the epidermis, and by absorption of light the body cells are activated, and hence increased oxidation of carbohydrates, fats, and proteins takes place. It seems to be accepted on all hands that several diseases are caused by defective metaboilism, and threfore sunlight should prove efficacious in the treatment of these diseases.

The results on the photo-oxidation show that under identical conditons butter is oxidised to greater extent than glucose in presence of sunlight. It is generally believed that rickets is associated with defective fat metaboilism and it is expected from our experimental observations that rickets would be more amenable to light treatment than diabetes as the oxidation of fat is more facilitated by light than that of glucose. Several medical men have reported that the metoboilism of children or adult exposed to light may be 40% higher than in the absence of light. Hence it can be concluded that light in the treatment of disease, is likely to act as a stimulant of body cells and accelerator of metabolism, as the oxidation of food material is accelerated by light.

Influence of Light on Plant Respiration.

Dhar and collaborators have shown that the food materials lke starch, sugars, proteins and fats in aqueous solutions or suspensioins are oxidised to carbon dioxidide and water by simply passing air at the ordinary temperature in presenee of sunlight. In absence of light, there is no oxidation. In presence of inductors like ferrous hydroxide, cerous hydroxide, glutathione, etc., the food materials are oxidised to carbon dioxide and water by air even in absence of light. In presence of sunlight these induced oxidations are greatly increased. It appears, therefore, that the sunlight absorbed by the plants will also accelerate the oxidation of glucose and other food materials present in the plant. Hence in presence of light the respiration in the plant is likely to be increased.

The experimental observations of Miss Matthaei (1905), Rose (1910) Shri Ranjan (1932), Parija and co-workers (1933) and others seem to indicate the accelerating influence of light on plant respiration.

The following observations can be explained from the view point that light accelerates respiration in plants:

The velocity of respiration of plants growing in shade is generally much less than in plants growing in light. Light retards growth and the higher the intensity of light, the greater the retardation. The retarding effect of light, on the aerial organs of plants is well observed on mountain tops, where the solar radiations are richer in ultraviolet radiations than in plains.

It is well known that not only higher temperature but also long exposure to strong light adversely affects photosynthetic activity. It appears that plants growing on mountain tops receive more ultraviolet radiations, which are less favourable for carbon assimilation than red light but ultraviolet light accelerates the ox idation processes markedly. Hence in presence of light rich in ultraviolet radiations, the accumulation of carbonaceous matter in plants due to photosynthesis and hence growth are likely to be less because of the intensification of the opposing process *i.e.*, respiration, by the absorption of light energy. Because of the enhanced respiration in presence of light, the growth of the plant is likely to be retarded. This effect seems to be allied to the phenomenon of " solarisation."

It is well known that when plants are cultivated under conditions of high light intensity, they utilise only a small amount of the absorbed energy for photosynthesis. Plants growing in presence of feeble light can convert a relatively larger proportion of the absorbed energy into carbonaceous compounds. This behavior appears to be due to the intensification of respiration partly by absorption of light and partly by increase of temperature caused by the absorption of the incident radiations when the light is strong. This enhancement of respiration will minimise the photosynthetic effect.

Moreover with increasing temperature, the " compensation point " should rise more rapidly than the velocity of respiration because of its additional enhancement by light absorption and this is clearly borne out from the experiments on *cladophora*, in which an increase of temperature from 5° to 25° causes the respiration to become 4·8 times greater when determined in the dark, whilst the light intensity increases 6·69 times for the compensation point.

It has been assumed by most of the plant physiologists that the process of respiration is not accelerated by light absorption but the foregoing considerations seem to prove that light also accelerates respiration in both plants and animals. Several other aspects of the

influence of light on plant respiration were discussed in my last address (*cf. J. Indian Chem Soc.*, 1934, 11, 145.)

Influence of Light on Ammonification and Nitrification.

In recent publications it has been shown that light plays an important rôle in the phenomena of nitrification and ammonification. Gopala Rao and Dhar (1931) have observed that ammonia is slowly oxidised in aqueous solution to nitrite, when exposed to the light from a quartz mercury vapour lamp and copper arc and more slowly in sunlight. The oxidation of ammonia solutions takes place even in light filtered through a 5% quinine sulphate solution of 4 cm. thickness, which cuts off radiations shorter than 4200 Å. Ammonium salts are also oxidised to nitrites, the reaction being slower in the case of the sulphate and chloride than with phosphate and carbonate.

The velocity of the photo-oxidation of aqueous solutions of ammonia and its salts is considerably increased by the presence of photosensitisers like titania, zinc, and cadmium oxides, alumina, silica, magnesia, etc. Titania is the most and silica is the least active in this photo-oxidation. The p_H of the solution has a profound influence on the reaction velocity; alkalinity increases the velocity of oxidation of ammonium salts and acidity decreases the oxidation. The velocity of the oxidation is greater in quartz vessels than in glass ones. The accumulation of nitrite appears to have no influence on the velocity of the oxdation of ammonia and its salts photochemically.

Recently Dhar, Bhattacharya and Biswas (1932-33) have shown that large amounts of ammonium salts are converted into nitrite and nitrate in presence of light and air but very little oxidation takes place in the dark when ammonium salts and sterilised or unsterilised soil are allowed to oxidise in air. It has been shown that the oxidation of ammonium salts mixed with sterilised or unsterilised soil in covered vessels coated with Japan black enamel (*i.e.* receiving no light) when kept in the sun along with the vessels receiving light is much smaller than in those exposed to light. If nitrification were mainly a bacterial process the amount of nitrification in the vessels in the dark with the unsterilised soil should not have been materially different from those exposed to light. We have made numerous comparative experiments like those on the oxidation of ammonium salts to nitrite and of nitrite to nitrate with both sterilised and unsterilised soil kept in light and in dark and we find that the formation of nitrite and nitrate is

always much greater in the vessels exposed to light than in those kept in the dark.

The photolysis of various amino acids in sunlight has been studied by Gopala Rao and Dhar (1934) and Dhar and Mukherji (1934). These amino acids decompose with the liberation of ammonia. The decomposition appears to be one of oxidative de-amination, because by passing oxygen or air through the solution of the amino acids the amount of ammonia liberated is increased. The aliphatic amino acids, *e.g.*, glycine are oxidised in the presence of air and sunlight with the formation of the corresponding aldehyde, ammonia and carbon dioxide. This is represented by the general equation,

$$R{\cdot}CH{\cdot}NH_2\,COOH + (O) \longrightarrow R{\cdot}CHO + NH_3 + CO_2.$$

In most of the cases, the amount of ammoniacal nitrogen formed by photolysis was found to correspond quantitatively to the decrease in amino-nitrogen.

In the light of the above experimental evidence, the author believes that the formation of ammonia in the soil from amino acids obtained from protein decomposition is mainly an oxidative de-amination, accelerated by sunlight. We have shown that aqueous solutions of amino acids photolyse in the presence of photo-sensitisers like titanium dioxide, aluminium oxide, humic acid, zinc oxide, etc. When we keep in mind that the first three substances normally occur in all soils, it will be clear that ammonification in soils can take place without the presence of bacteria or fungi, if only sunlight be present.

Recently it has been observed by us that dilute solutions of sodium or potassium nitrite are almost completely oxidised to nitrate when exposed to light along with solid substances like TiO_2, ZnO, Fe_2O_3, and sterilised soil in the absence of bacteria. In other words, from the experimental work carried on in these laboratories, we find that not only are ammonium salts oxidised to nitrite by air in the presence of light but the nitrites are also in their turn, readily converted into nitrate when exposed to light and air along with sterilised soil or photocatalysts. It seems, therefore, that the whole process of nitrification can be photochemical. Moreover, it has been found by us that solutions of amino acids are readily oxidised to ammonia in the presence of air and light. Thus one of the important stages in the process of ammonification is also markedly accelerated by light.

Leather working at Pusa (India) stated that the maximum temperature at Pusa may rise to 70° at the soil surface and 60° at a depth of 1 or 2 inches. In Egypt the recorded temperature is 65° at the surface and 56° at a depth of 2 inches. Similar high temperatures have been recorded in the summer months at Allahabad. The measurements of S. P. Tandon and N. R. Dhar (1934) show that 35° is the optimum temperature for bacterial nitrification, which becomes practically negligible at 50°. Hence in tropics, nitrification in soil cannot be to any marked extent, of bacterial origin in the months of April, May, June, and July, when the soil temperature is much greater than the optimum for nitrification by bacteria. In these very months the amount of nitrate in soil is, however, the greatest. Even in colder countries, like England and Germany, the soil temperature may rise to 35° or more in summer, although the optimum temperature for bacterial nitrification is stated to be 25° in the cold countries. In these countries bacterial nitrification must be greatly reduced in the summer months as a result of the soil temperature becoming much greater than the optimum temperature for bacterial nitrification, though the nitrate content of the soil in these countries is also largest in the summer time.

It is believed that in moist soils, most of the bacteria are concentrated in the first 2 feet of the soil. The largest numbers are observed 1 to 3 inches below the surface. Because of the antiseptic properties of the solar radiations and the rapid evaporation of moisture from the soil surface, the number of bacteria is less on the surface. According to Waksman, (1916) soils under shade have the highest number of bacteria at a depth of 1 inch, and the number decreases with depth, whereas soils receiving sunlight contain the largest numbers of bacteria at a depth of 4 inches.

It is generally agreed that nitrification is most active at the surface of the soil. According to Prescott and Piper (1930) nearly 80% of the nitrate accumulation takes place in the first 3½ inches of the soil from the surface. From the observations recorded above it seems to us that the soil temperature in the summer months in tropical countries must not be much below 50° even at the depth of 3½ inches from the surface, although the bacterial nitrification has the optimum temperature of 35°. In Lyallpur, Punjab, in summer months, the soil temperature at 5 cm. depth is as high as 50° and at 30 cm. depth 37°. It appears, therefore, that in the first 3½ inches of the soil, where there is maximum nitrification as observed by

different investigators, very few bacteria can exist in tropical countries in summer months, although the amount of nitrate in soil is maximum in summer. We are led to conclude, therefore, that agencies other than bacterial must be active in causing nitrification, which is going on at a maximum speed in the soil in summer months within 3½ inches of the soil. As we have observed that light markedly accelerates the oxidation of amino acids to NH_3, of ammonium salts to nitrites, and of nitrites to nitrates, and that all these oxidations are accelerated by increase of temperature, we are led to believe that light absorption and increase of temperature play a more important rôle than bacteria in nitrification in summer months, when the nitrate content of the soil is known to be maximum in almost all countries.

The increase in fertility of soil as a result of exposure to sunlight as practised in India, Egypt, and other countries from time immemorial can be easily explained from our observations. The increased production of ammonia and nitrate by partial sterilisation of soil has been stated by authorities on agriculture to be not a necessary consequence of the higher number of the organisms present on the soil. As nitrification is essentially an oxidation reaction taking place on the soil surface, the various agencies, *e.g.*, increase in the aeration, soil surface, the temperature upto a limiting value, will increase nitrification. Moreover, sunlight or diffused light is always available and accelerates the formation of NH_3 from amino acids, and the oxidation of NH_3 to nitrite and of nitrite to nitrate. It appears, that the increase in fertility of soil on heating or exposure to sunlight, as is done by cultivators in many countries, is mainly due to increased oxidation of nitrogenous compounds, especially of the amino acids, causing the formation of NH_3 and to increased nitrification brought about by the soil becoming more porous and by the accentuation of the air supply and above all by the increased light absorption. When a soil is ploughed, fresh surfaces are exposed to sunlight and air and ammonification and nitrification are facilitated. In this connection, the following statement of Russell (1932) is of interest:—"Ammonia production in soil, however, is not entirely the result of direct action of micro-organisms. It goes on even in presence of antiseptics."

It is gratifying to find that our obsesvations on the influence of light on soil processes are being corroborated by workers in different tropical stations. Thus Sarkaria and Fazal Uddin (Lyallpur, 1933) have observed marked ammonification and nitrification of several nitrogenous

compounds and nitrification of ammonium salts and oxidation of sodium nitrite to nitrate in presence of sunlight aided by photocatalysts in the absence of bacteria. It is of interest to record here the following observations of two bacteriologists regarding the influence of light on these soil processes in the tropical climates:—"I have been particularly interested in your very informative papers on the subject on photochemical nitrification which have come to my attention these recent years. The general underlying theory of your work is quite in harmony with some of the work I have been carrying on since my arrival in Hawaii. My early studies in nitrification of ammonium sulphate fertilisers in some of our Hawaiian soils were not explainable from a bacterial standpoint. The application of the photochemical idea is proving a very worthwhile venture" (Allen, University of Hawaii). "From my experience in Malaya, where I was particularly struck by the paucity of soil micro-organisms, I should think your results on photonitrifi cation are of quite general application in tropical countries" (Corbet, Agricultural Researches Station Bracknell, Berkshire).

Denitrification in Sunlight and its Retardation.

The researches of different investigators show that nitrogen in the gaseous state is lost from soils when the conditions are favourable for oxidation. The loss of nitrogen in this process may be double the amount of nitrogen taken up by the plant grown on the soil.

A greater loss of nitrogen is observed when a manure is composted under ærobic than anærobic conditions. There is more loss of nitrogen from stable manure in presence of nitrifying bacteria than in their absence. It has also been reported that in the nitrification of different oil-cakes, the loss of nitrogen is the greatest with the most easily and quickly nitrifiable cakes. Greater velocity of oxidation and greater nitrogen loss have been observed with ammonium salts than with farm-yard and green manures on nitrification. Moreover, when there is a large amount of carbonaceous matter present in the manures along with nitrogenous compounds, the velocity of the oxidation of nitrogenous compouds and the amount of nitrogen loss are also decreased.

Experiments carried on at different places show that the total amount of nitrate present in soils containing crops is less than that in neighbouring fallow soils even when a correction is applied

for the amount of nitrate taken up by the crop. The oxidation processes are more vigorous in soils with crops than in those without them.

Our experimental results show that the loss of nitrogen on exposing ammonium salt solutions to light and air is always greater in light than in the dark. The oxidation of ammonium salts by air is greater in light than in the dark and hence the formation and decomposition of ammonium nitrite is greater in light than in the dark. Moreover, solutions of ammonium chloride and sodium nitrite decompose readily with evolution of nitrogen when exposed to sunlight in open beakers mixed with sterilised and unsterilised soils. This decomposition is considerably less in dilute solutions of ammonium nitrite and also when cane sugar is added to the solution containing ammonium and nitrite ions.

All these observations have been explained from the view point that in the processes of ammonification, and nitrification taking place in the soil or in solutions, ammonium nitrite is produced. Solutions of ammonium nitrite have been found to be decomposed into nitrogen and water readily by increase of temperature or exposing them to light. The formation of ammonium nitrite from ammonium salts or proteins requires oxygen and that is why, this type of dinitrification is facilitated by increased soil aeration and also soil acidity as nitrous acid also undergoes decomposition according to the equation,

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

Addition of carbonaceous substances like molasses tends to preserve the soil nitrogen by decreasing the velocity of the oxidation of the nitrogenous compounds present in the soil and thus decreasing the probability of the formation and decomposition of ammonium nitrite.

Of course, too little oxidation of the protein present in the soil by the addition of molasses will not make the soil suitable for the growth of crops. It seems necessary that an equilibrium should be established between the oxidised and the unoxidised proteins, ammonium salts and other nitrogenous substances, which are present in the soil for maintaining its fertility at a proper level. Too much oxidation of the nitrogenous substances, and ammonium salts may entail marked nitrogen loss by this type of dinitrification, and too little oxidation will not make the soil fertile enough for a good

yield of crop. Hence the molasses should not be added in very large amounts and after the addition of molasses, the soil should be ploughed several times to help oxidation. Moreover, molasses when added to soil in moderate amounts and the soil is properly aerated for helping the oxidation reactions, cause nitrogen fixation as evidenced by the increase of ammoniacal nitrogen content of soil.

Nitrogen Fixation in Soils by the Application of Molasses.

Our results obtained with soil and cane sugar on exposure to sunlight and air show that both with sterilised and unsterilised soils, the ammoniacal nitrogen goes on increasing upto a limiting value with time, although the nitric nitrogen remains constant during this time. After this period further exposure to light leads to a decrease in ammoniacal nitrogen and an increase of nitric nitrogen but the sum of the ammoniacal and nitric nitrogen is less than that obtained before. This behaviour is due to a loss of nitrogen caused by the photochemical and catalytic decomposition of ammonium nitrite formed on the soil surface. It is well known that 90% of the nitrogen fixed by Azotobacter exists as ammonia, and that is why the ammonia increases when the unsterilised soil is exposed to light mixed with sugar. It is surprising that even in the sterilised soil ammonia goes on increasing. Both the soils were tested bacteriologically after exposure for Azotobacter, which was readily obtained in the unsterilised soil. After culture only a few could be detected in the sterilised ones. It seems that the combination of nitrogen and oxygen is induced by the oxidation of sugars present in the soil. The nitrite and nitrate formed are readily reduced to ammonia by the reducing action of the sugars, and that is why only ammonia is increased and not nitrate. In a recent communication from this laboratory it has been shown that the optimum temperature for nitrogen fixation by Azotobacter is 35°, whilst at 45° practically no nitrogen fixation by Azotobacter takes place. It seems, therefore, that the nitrogen fixation during summer days by bacteria will be exceedingly small because they will be mostly killed by the intense heat and light which the soil receives. Our results show that the fixation of nitrogen in the soil by the addition of sugar is helped by light and may take place even in the absence of Azotobacter. In the absence of bacteria, hardly any fixation of nitrogen in the soil takes place in the dark.

After obtaining definite evidence regarding the fixation of nitrogen by the addition of sugar both in the sterilised and unsterilised soils, we extended our experiments on the fixation of nitrogen under ordinary field conditions by the addition of molasses. 35 Kilos of molasses were added to an area of 500 sq. ft. and the area was divided into two parts, one part was dug several times after the addition of molasses and the other part was not ploughed.

Our observations show that the ammoniacal nitrogen is about 10 times greater in soil after the addition of molasses and aeration even when correction is applied for the addition of ammonia added with molasses. The nitrogen fixed in the soil on the addition of carbohydrates, exists chiefly as ammonia and hence the ammoniacal nitrogen content of a soil is higher on the addition of molasses. From these experiments it can be concluded that considerable fixation of nitrogen takes place in tropical soils on the addition of molasses provided the aeration of the soil is sufficient. When the aeration is incomplete nitrogen fixation becomes defective because energy is necessary for nitrogen fixation and this energy comes from the oxidation of sugars and that is why a large supply of air is necessary. In the absence of air, anærobic bacteria and fungii flourish and utilise the carbohydrates and nitrate for their growth and hence in the presence of bacteria, instead of addition of nitrogen to soil, nitrate is lost, as has been observed by different people. Moreover, this oxidation is facilitated by increase of temperature and sunlight and hence there is a great possibility for the utilisation of molasses in India as a manure in increasing the soil nitrogen, which is the crying need of tropical soils, provided there is sufficient aeration and the soil is exposed to sunlight. The carbohydrates present in molasses will undergo oxidation in the soil liberating energy necessary for the fixation of atmospheric nitrogen. Thus by the addition of carbohydrates the soil fertility with regard to combined nitrogen can be easily increased. If the acidity of the soil is increased on the addition of molasses, some calcium carbonate has to be added to the soil for the neutralisation of the acid. It is found that the growth of wheat is the best on the portion of the soil containing molasses and well turned over and on the portion containing molasses but not aerated, the growth seems slightly inferior to that on the portion containing no molasses but well aerated by digging.

Many workers have failed to obtain nitrogen fixation in soils on the addition of carbohydrates. It seems that the failure is mainly due to

the insufficiency of aeration in the soil. In cold countries, the velocity of the oxidation of the energy rich substances present in the soil may be very small and thus the energy available from the oxidation of sugar may be too small for marked nitrogen fixation. In tropical countries, however, if the soil is well ploughed after the addition of carbohydrates, there is no reason, why the soil fertility regarding combined nitrogen should not be increased.

I have begun my address with a dictum of Lavoisier and it is fitting that I should end it with the following lines written by the great French Chemist not long before his tragic end by the guillotine:—

"To merit well of humanity and to pay tribute to one's country it is not necessary to take part in brilliant public functions that have to do with the organisation and regeneration of empires. The naturalist may also perform patriotic functions in the silence of his laboratory and at his desk; he can hope through his labours to diminish the mass of ills which afflict the human race or to increase its happiness and pleasure; and should he by some new methods which he has opened up prolong the average life of men by years or even by days he can also aspire to the glorious title of benefactor of humanity."

Effect of Polarity on the Solubilities of some Organic Acids.

By P. G. Desai and A. M. Patel.

It has been claimed by Walden (*Z. physikal. Chem.*, 1906, **55**, 708) that the solubility of a salt in a series of solvents is greater, the greater the degree of dissociation, *i e.*, the more marked the polar character.

The dielectric constant is the most direct evidence of polarity. The magnitude of this constant, therefore, indicates the moment of the polar groups within the liquids or the displacement of electrons or both. The electric moment depends upon both the magnitude of the charge and the length of the dipole.

In order to establish a relationship between the polarities of the solvents and the solutes, it is essential that a systematic study of the solubilities of substances with increasing polarity in a series of solvents of decreasing polarity should be made. Much data which are found in the literature are rather inadequate from this point of view and therefore the present work was undertaken.

Experimental.

Conductivity water was used throughout the work. The organic solvents were purified by distillation at their known boiling points, whereas the solutes were twice recrystallised. Jena glass materials were used in the experiments and before their use they were thoroughly washed with chromic acid, rinsed with conductivity water and finally steamed.

Procedure.—100 C.c. of the solvents were saturated with organic acids in a series of flasks, which were kept revolving on a wheel in an air thermostat at 28° for 48 hours. At the end, the solutions were filtered. In order to avoid any error due to the absorption of the solute by the filter paper, 100 c.c. of a fresh saturated solution were filtered through it before the solution used for the estimation of the acid was passed through. As the undissolved acid

did not completely settle down, it was found impossible to pipette out a certain amount from the flask itself. A suitable amount of the filtrate was then titrated against $Ba(OH)_2$ solution using phenolphthalein as an indicator. It was found by blank experiments that this method gave very reliable results, the error being less than 0·5%. Three readings were taken in each case and the mean was taken. Before the beginning of the experiments, the stock-solution of $Ba(OH)_2$ which was made free from any insoluble carbonate, was titrated against a standard solution of succinic acid. The hydroxide solution was also protected from being contaminated by air during the experimental work.

In the following tables, the solubilities are expressed in four different ways, *viz*, (*i*) in g./100 c.c. of the saturated solution, (*ii*) g./100 g. of the saturated solution, (*iii*) g./100 g. of the solvent, and (*iv*) in mol-fractions.

The densities of the saturated solutions were measured by means of a pyknometer. The densities taken are the mean of the three readings. The solubility in mol-fraction is calculated by the following:

Mol-fraction $= N = \frac{n_1}{n_1 + n}$, where n_1 is the number of mols of the solute in solution and n_2 is the number of mols of the solvent in solution.

The ideal solubility was calculated from the following equation (Hildebrand, " Solubility " 1924)

$$\log N = \frac{-Lf}{4{\cdot}58} \left(\frac{1}{T} - \frac{1}{T_m} \right)$$

N is the solubility of mol-fraction, Lf is the heat of fusion of the solute, T is the absolute temperature at which the ideal solubility is calculated, T_m is the absolute temperature of the melting points of the pure solute.

In the following table, the solubilities of benzoic, salicylic, phthalic, succinic and cinnamic acids in terms of "mol fractions" and the dielectric constants at 25° of the various organic solvents are given. The latter values have been taken from Landolt-Bornstein "Tabellen" and also from Dobrosserdow (*J. Russ. Phys. Chem. Soc.*, 1910, **41**, 1164, 1385).

TABLE I.

Solubilities of different solutes in various solvents in "mol fractions" at 28°.

Solvent.	Dielectric const. at 25°.	Solubility of benzoic acid.	Solubility of salicylic acid.	Solubility of phthalic acid.	Solubility of succinic acid.	Solubility of cinnamic acid.
Water	81·00	0·0005685	0·0003118	0·0008724	0·01460	0·0000894
Hexane	1·85	0·01399	0·00111	—	—	—
Carbon tetrachloride	2·21	0·0593	0·003803	0·0000244	0·0000118	0·01071
Benzene	2·27	0·06191	0·005441	0·0000447	0·00002824	0·03033
Toluene	2·34	0·08553	0·006052	0·0000469	0·0000298	0·02966
m-Xylene	2·35	0·0889	0·006554	0·0000465	0·0000304	0·02852
Chlorobenzene	11·0	0·1047	0·007903	0·0000577	0·0000476	0·03608
Nitrobenzene	36·0	0·1081	0·02509	0·0000898	0·000128	0·04965
Chloroform	5·1	0·1495	0·02679	0·000184	0·000138	0·07268
Methyl alcohol	32·0	0·1689	0·1252	0·05125	0·05620	0·06337
Ethyl alcohol	25·0	0·1882	0·1479	0·04265	0·04865	0·07665
n-Propyl alcohol	22·0	0·1810	0·1438	0·02732	0·03613	0·0850
n-Butyl alcohol	19·2	0·1968	0·1588	0·02231	0·02618	0·09156
Acetone	21·0	0·2141	0·1906	0·02896	0·02948	0·11930

The solubilities of different acids were calculated in g. per 100 c.c. solution and also in g. per 100 g. of the solution. However, it was noticed that these methods of calculation did not show any sign of uniformity when they were compared with the dielectric constants of the organic solvents. Thus, it was realised that before any comparative study of the solubilities of different substances is attempted, it is advisable to select only one method for expressing solubilities. Hildebrand ("Solubility" New York, 1924) rightly believes that "a gram molecule or mol has always greater significance to the chemist than any other of the amount of a substance." Greater importance is, therefore, attached in this paper to the solubilities expressed in mol fractions and they are made the basis for the subsequent interpretation of the results.

In Table I are given the solubilities of benzoic acid in fourteen solvents of varying polarities. As the solute is partly polar and partly non-polar, it will be expected that its solubility will be less in highly polar and non-polar solvents and greater in the intermediate solvents. The ideal solubility is reached in ethyl alcohol. It can be seen from the table that the order of the solubilities in different solvents is in accord with their dielectric constants. However, chloroform and normal butyl alcohol show an exception to the general behaviour. This is due to the fact that chloroform forms complexes with ether-oxygen and carboxyl-oxygen (Hildebrand, "solibility," 1924, p. 158) and therefore it acts as a better solvent than would otherwise be expected. In the case of butyl alcohol, the ideal solubility seems to have been exceeded on account of the formation of loose complexes with the solute.

The solubilities of salicylic, phthalic, succinic and cinnamic acids in all the fourteen solvents are also given in Table I. Their polarity is in the following decreasing order:—

Succinic acid $\geqslant$ phthalic acid $>$ salicylic acid $>$ cinnamic acid $>$ benzoic acid.

From the results obtained, it can be seen that the solubilities of different substances in solvents of varying degrees of polarity, as evidenced by their dielectric constants, are in accordance with their polarity and that of the organic solvents.

From the order of the polarity of the solutes, it will be expected that their solubilities in non-polar solvents, such as hexane, carbon tetrachloride and others, will be greater as one passes from succinic acid to benzoic acid. Secondly, in accordance with the polarity of

these solvents, as seen from their dielectric constants the solubilities of the different solutes should increase, the order being :—

Hexane < carbon tetrachloride < benzene < toluene < *m*-xylene.

These expectations are fulfilled, as can be seen from the table, except in the case of cinnamic acid, where the order of the solvent action of the aromatic hydrocarbons is reversed.

In accordance with their polarity, the ideal solubilities of the acids will be reached either in methyl or methyl alcohol. Comparing their solubilities in methyl alcohol, the following order is obtained :—

Phthalic < succinic < cinnamic < salicylic < benzoic acid.

This is truly very strange. However, these results can be clearly explained if it is assumed that the last three acids become associated with or form loose alcoholates with the solvents, whereas the first two do not.

As mentioned above, it should be expected that the solubilities of all the acids in water should be less than those in nitrobenzene. From the table, it can be seen that this expectation is fulfilled by the solubilities of benzoic, cinnamic and salicylic acids, while those of phthalic and succinic acids are greater in water than those in nitrobenzene. This can only happen if these two acids become associated with water. Oxalic acid being more polar than succinic acid, crystallises with two molecules of water from its aqueous solution. It is, therefore, not unreasonable to assume that phthalic acid with two adjacent carboxyl groups and succinic acid with two carboxyl groups separated by the two methylene ones, should form hydrates with water, which may not be stable enough to be separated.

Thus, it can be seen that the solubility as expressed in mol-fraction of any solute is largely dependent upon the mutual polarity.

From the above study, predictions of solubility can be made. Thus, one can say that the acids studied will be more soluble in heptane, octane or nonane than in hexane, as the dielectric constant of the latter is smaller than that of any one of the former. Their solubilities in bromoform, ethyl chloride, ethyl ether, terpeneol and bromobenzene will be less than those in either methyl or ethyl alcohol. Glycol, being more polar than nitrobenzene, will be a poorer solvent for all the acids studied, whereas aniline, which is slightly polar and more basic, should be a better solvent than nitrobenzene. Pyridine, being more polar, will be a better solvent than piperidine

and quinoline. The solubilities of the acids will increase with the higher homologues of benzene.

The order of the solubilities of different acids in comparatively non-polar solvents can also be predicated with a fair degree of accuracy, depending upon the polar nature of solute. The greater the increase in the number of the polar substituents, such as OH, NO_2, NH_2, COOH, in the substituted benzoic acids, the less is the solvent action of non-polar liquids.

Predictions of the solubility in more polar solvents, such as alcohols and others, are beset with difficulties on account of the fact that many times 'solvates' are formed. However, one can say that if the ideal solubility is reached in ethyl alcohol, its higher homologues will be poorer solvents as well as methyl alcohol.

Summary.

1. The solubilities of benzoic, cinnamic, salicylic, phthalic and succinic acids have been determined in fourteen solvents of varying degrees of polarity.

2. It has been shown that the expression of solubility in mol-fraction is a more rational method.

3. It is found that the solubilities in very slightly polar solvents decrease with increasing polarity of the solute, the solubilities of phthalic and succinic acids being negligible in these solvents.

4. The order of solubility is in accordance with the polarity of the solvents in the case of the aromatic hydro carbons, hexane and carbon tetrachloride, while in the case of more polar substances, the order is not well defined.

5. It is found that chloroform behaves abnormally with all solutes, while acetone and *n*-butyl alcohol do so in some cases.

6. It has been inferred from the solubilities of acids in water, nitrobenzene and alcohols, that benzoic, cinnamic and salicylic acids form loose 'alcoholates' with the solvents, whereas succinic and phthalic acids form hydrates with water.

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The Reaction between Iodine and Oxalic Acid in Ethylene Glycol as a Solvent (A Preliminary Note).

By B. K. Chatterjee and B. L. Vaishya.

The reaction between oxalic acid or an oxalate and iodine has been much studied by Dhar and co-workers (*cf.* Dhar, "The Chemical Action of Light." p. 156), by Berthoud and Bellenot (*J. chim. Phys.*, 1924, **21**, 308) and very recently by Griffith and McKeown (*Trans. Faraday Soc.*, 1932, **28**, 518) in water as the medium. Difference in opinion, however, exists between the various workers as to the exact mechanism of the reaction. The present authors, therefore, made an attempt to study the reaction in a non-aqueous solvent, *i.e.*, ethylene glycol, but all attempts to make these react in the solvent, have been fruitless.

The reaction was studied both in dark and in light from a thousand watt lamp of tungsten filament in presence as well as in absence of water. The percentage of water used was 50 and 30 of the reaction mixture by volume. The substance failed to react even in presence of water,

The reactions were carried out at 31°. When attempts were made to study the reaction at high temperatures it was found that iodine attacked the solvent (glycol).

The results show that although iodine and oxalic acid are soluble in glycol yet they fail to react in the dark as well as in the total light from a thousand watt lamp. This is a curious phenomenon considering the fact that in water these two substances react with a measurable velocity. Our experiments prove, however, that the reaction between oxalic acid and iodine is truly ionic in character. According to Berthoud and Bellenot (*loc. cit.*) the following reactions take place in water.

$$I_2 + h\nu \longrightarrow 2I \quad \ldots \quad \ldots \quad \ldots \quad (i)$$

$$I + K_2C_2O_4 \longrightarrow KC_2O_4 + KI \quad \ldots \quad \ldots \quad (ii)$$

$$KC_2O_4 + I_2 \longrightarrow 2CO_2 + KI + I \quad \ldots \quad \ldots \quad (iii)$$

$$2I \longrightarrow I_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (iv)$$

From the above equations it will be seen that the reaction is independent of the medium, *i.e.*, the water does not enter into the chemical equations. If this were the case, the reaction should have taken place even in glycol.

From this point of view, the views of Griffith and McKeown (*loc. cit.*) seem to be correct (*vide infra*). According to them the reaction although truly ionic is not independent of the medium. Iodine is transformed first to IOH before it enters into the reaction,

$$HC_2O_4 + 2OH \longrightarrow H_2O + 2CO_2 + I.$$

But this raises the important question why the iodine-oxalic acid mixture in glycol fails to react even in the presence of water, or in what way does the glycol prevent the ionisation (if this is the primary process) of both the reactants. In the opinion of the authors the molecules of iodine as well as those of oxalic acid are closely surrounded by clusters of glycol molecules and although glycol itself is soluble in water, in presence of water, these clusters or structures are not sufficiently separated from the iodine or oxalic acid molecules for them to ionise as in aqueous solution. It is strange that both heat and light fail to ionise their molecules in glycol.

Glycol is very similar in properties to water. Almost all substances soluble in water are soluble in glycol also. Moreover, it contains in its molecule two 'OH' groups and its electrical conductivity is slightly greater than that of water (Critical Tables, Vol. VI, pp. 142, 152). If IOH formation is the primary process there is a greater chance of its formation in glycol than in water. Water itself is only slightly ionised. Hence if IOH formation is favoured in glycol, the reaction ought to be faster in glycol than in water. The above experiments have proved definitely that the reaction between oxalic acid and iodine is not independent of the medium in which it is carried out. The medium should be such that ionisation of the reactants must take place. The formation of an intermediate compound seems evident. The nature of the intermediate compound is not yet evident to the authors, but the suggested view of IOH formation is certainly doubtful,

A more exhaustive work is being carried out in these laboratories in which the action of the solvents is being studied.

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Mercuration of Coumarins (A Note).

By Dukkhaharan Chakravarti.

Naik and Patel (*J. Chem. Soc.*, 1934, 1043) have mercurated coumarin derivatives '*with mercuric acetate in aqueous solution through the neutral sodium salt.*' They have not made any reference to the work of Sen and Chakravarti (*J. Indian Chem. Soc.*, 1929, 6, 847; 1930, 7, 247) probably through oversight, though the method of preparation is exactly the same. We described the mercuration of coumarin, 7-hydroxy-4-methylcoumarin, 4:7-dimethylcoumarin, 6-aminocoumarin, 7:8-dihydroxy-4-methylcoumarin, 4:6-dimethylcoumarin and also studied with interesting results the influence of substituents on the coumarins in mercuration by two different methods, (*a*) with yellow mercuric oxide and, (*b*) with mercuric acetate. Some of the compounds described by Naik and Patel are widely different from our compounds and as this work negatives in some cases the conclusions reached by us, it is necessary to record the following facts.

(1) 6:8-Bisacetoxymercuricoumarin (decomp. 248°) has been obtained by Naik and Patel by the mercuration of coumarin, whereas it was found by Sen and Chakravarti (*loc. cit.*) that the mercury compound, thus obtained, is diacetoxymercuri-*o*-coumaric acid (decomp. 215°), as it gives *o*-coumaric acid (m. p. 207-9°) and as the same mercury compound of *o*-coumaric acid (decomp. 215°) is obtained by mercuration of *o*-coumaric acid.

This is a convenient method for the preparation of *o*-coumaric acid and this has been admitted by Dey, Rao and Seshadri (*J. Indian Chem. Soc.*, 1934. 11, 745). It is also significant to note that Naik and Patel's compound is '*soluble in dilute sodium hydroxide solution.*'

(2) According to Naik and Patel the effect of substituents on the mercuration of coumarins by mercuric acetate is extraodinary since in 6-nitrocoumarin the nitro group is knocked off and 6:8-diacetoxymercuricoumarin is obtained. It has been found by us that 6-nitrocoumarin gives 5-nitro-*o*-coumaric acid, identical with the nitro-*o*-coumaric acid, prepared by Dey and Row (*J. Chem. Soc.*, 1924,

125, 561). This observation has also been supported by Dey, Rao and Seshadri (*loc. cit.*), who record "though the use of mercuric acetate resulted in a better yield (of 5-nitrocoumaric acid) the product obtained was rather impure and required several crystallisations."

Incidentally it may also be noted that whereas 6-aminocoumarin produces 6-acetoxymercuriaminocoumarin with mercuric acetate where the mercury atom replaces the hydrogen in the amino group (Sen and Chakravarti, *loc. cit.*) Naik and Patel have obtained 7-amino-6:8-bisacetoxymercuri-4-methylcoumarin from 7-amino-4-methylcoumarin and have given no experimental evidence that the compound possesses a free NH_2 group.

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Geometrical Inversion in the Acids Derived from Coumarins (A Note).

BY BIMAN BIHARI DEY, RUBUGUNDAY HARI RAMCHANDRA RAO AND TIRUVENKATA RAJENDRA SESHADRI.

In connection with the paper on the above subject (*J. Indian Chem. Soc.*, 1934, **11**, 743) it was found necessary to give fuller details of certain experiments and to correct certain errors that had crept in during the course of publication.

7-Methoxycoumarin was obtained in a rather poor yield (1·5 g.) from umbelliferone (4 g.) by methylation in the ordinary way with dimethylsulphate in the presence of caustic alkali. A better yield (2·8 g.) was produced when the methylation was effected in benzene solution (boiling for 2 to 3 hours) in the presence of excess of anhydrous potassium carbonate. The decanted solution was distilled to remove the solvent and the residue was crystallised from methanol, m.p. 117-18°. But the easiest method for preparing the methoxycoumarin was from monomethylresorcinol which was itself made as below:

Resorcinol (11 g.) dissolved in a 10% solution of caustic soda (40 c. c.) was gradually treated at 60-70° with dimethyl sulphate (13 g.) accompanied by vigorous shaking. The reaction was completed by heating on a boiling water-bath for half an hour. The upper layer of oil was separated, the lower aqueous layer twice extracted with ether, the ether extract distilled, the resulting oil added to the main portion and the whole distilled in steam. The distillate was shaken up with ether and the ether solution extracted with 10% aqueous caustic soda. Monomethylresorcinol was thereby taken into the alkaline solution leaving behind in ether any dimethyl ether that might have been formed. The alkaline solution was acidified, ether exracted and the ether solution dried over calcium chloride. The monomethyl ether obtained after removing the solvent was purified by redistillation. It was a colourless liquid with a pleasant smell, boiling at 242-43°, yield 7·5 g. The condensation of the monomethyl ether with malic acid has already been described.

Action of Sunlight on the trans *Acids and their Esters.*

o-Coumaric acid.—After exposing the alcoholic solution to sunlight, alcohol was distilled off. The residue was dissolved in ether and the ether solution shaken with small quantities of 5% aqueous sodium bicarbonate till the aqueous layer became perfectly colourless and nonfluorescent thereby indicating complete removal of all unchanged acid. The ether solution was then washed with water, dried over calcium chloride and finally evaporated in a tared flask. The residue (coumarin) was weighed after drying in an evacuated desiccator over sulphuric acid for 24 hours, yield 65% after 24 hours' exposure and 48% after 6 hours' exposure.

In the case of the esters of *o*-coumaric acid the procedure was the same except that 2% aqueous caustic soda was used for removing unchanged esters from the coumarin formed. Methyl ester underwent 87% conversion in 24 hours and 54% in 6 hours whereas the ethyl ester underwent 74% conversion in 24 hours.

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Composition of Prussian and Turnbull's Blues. Part III.

By Abani K. Bhattacharya.

It has been shown in a previous communication (*Z. anorg. Chem.*, 1933, **213**, 240) that Prussian and Turnbull's blues tend to assume a similar composition on account of the mutual oxidation and reduction involved in the reaction between ferric and ferrocyanide ions in the preparation of the former, and between ferrous and ferricyanide ions in the preparation of the latter compound. Support to this view has been adduced by quantitative estimations of iron and cyanogen contents in Prussian and Turnbull's blues prepared under various concentrations of iron and ferrocyanogen salts, and by studying the change of their composition with time. It has also been qualitatively shown (*J. Indian Chem. Soc.*, 1934, **11**, 325) by examining the filtrates that mutual oxidation and reduction do take place under certain conditions between the reactants.

In this paper an attempt has been made to elucidate further the nature of the compositions of Prussian and Turnbull's blues through the absorption spectrographic study of the solutions of these substances in a suitable solvent and correlate the spectrographic observations with those already published in the previous communications.

Experimental.

Standard solutions of ferric chloride, ferrous sulphate, potassium ferro- and ferricyanides were prepared. Respective solutions of known molecular concentrations were mixed with each other in equivalent proportions and the precipitates filtered for preparing fresh Prussian and Turnbull's blue in 24 hours. In the case of the aged preparations, the reacting solutions after being mixed together were allowed to age for about five weeks in stoppered bottles. The precipitates of Prussian and Turnbull's blues thus prepared either fresh or aged, were washed free from soluble impurities with cold or slightly tepid distilled water and dried in a current of hot air. The dried precipitates were then estimated for Fe_2O_3 by direct decomposition with heat in a porcelain crucible and the solution of the Prussian or Turnbull's blue was made in oxalic acid ; the strength of the solution thus prepared was equivalent to 0·005 g. of Fe_2O_3 in 100 c.c. of oxalic acid containing 1·5 g. of $H_2C_2O_4,2H_2O$.

Absorption photographs were at first taken in the visible region with a constant deviation spectrograph (Adam Hilger's) by passing parallel rays from a point-o-lite source through the solution of Prussian or Turnbull's blue filled in a Baly's tube ; copper arc was taken on the plate as a reference spectrum to determine the wave-length where absorption had begun. From these photographs it appeared that the absorption shown by these substances was of a general, rather than selective character ; but on taking absorption photographs in the extreme red region it appeared that the absorption was selective and not general as was shown by the reappearance of the absorption band in the extreme red region, and for this reason it became necessary to study the absorptive properties of these substances in the visible, infra-red and ultraviolet regions.

The second set of photographs were taken with a grating spectograph on panchromatic and infra-red sensitive plates. When infra-red sensitive plates were used the grating camera was exposed to the second order spectrum, the effective rays of the first order being cut off by placing a yellow filter on the slit. A tungsten filament lamp was used as a source in this case and the rays rendered parallel by a lens were allowed to pass through various thicknesses of the solution in the Baly's tube and photographs taken. Copper arc was taken as standard for reference; and for each absorption spectrum of the solution, that of the solvent was taken side by side for the same thickness, in order to discover the region where absorption due to the soluble substance actually began. Time of exposure for the solution was ten times that for the solvent, for reasons which have been discussed later. The point of equal intensities on the spectra of solvent and solution was observed under a comparator and its distance from a standard line on the photographic plate was measured. Then the wave-lengths where absorption took place were calculated from the dispersion curve of the instrument. Absorption photographs were taken in the same manner in the ultraviolet region by means of a quartz spectrograph (Zeiss) using excited hydrogen tube as a continuous source of light. The thicknesses of solutions have been taken in most cases in the order 1·0, 1·3, 1·65, 2·15, 2·8, 3·6, 4·6, 6·0, 7·7, and 10 cms. successively in a 10 cm. Baly's tube, because with such thicknesses the values of log K increased uniformly by about 0·1 unit with increasing thicknesses of the solutions, and therefore, the points are more conveniently plotted.

It is known quantitatively that in the case of solutions the fractions dI/I of the intensity of light absorbed by the solution is proportional to its thickness or the number of dissolved molecules, *i.e.*—$dI/I = K'.c.dD$, where D is the finite thickness of the layer and c the concentration of the solution. Hence, for a particular concentration c and thickness D of the solution, if we observe a point on the plate where the intensity of light through the solution has been weakened to one tenth, then we get the well known relation, $K = I/cD$, where c is given in mol /litre and D in cm. and K is the absorption coefficient of the substance.

On evaluating K as above from c and D and finding out λ from the dispersion curve as aforesaid, values of log K were plotted against the corresponding values of λ and the absorption curve for each solution thus obtained. The time of exposure for the solvent was, therefore, allowed one tenth of that of the solution, so that the point where equal intensities would appear on the spectra of the solvent and solution, it became evident that the intensity of light through the solution had been weakened to one-tenth and hence the formula $K = cD$ could be applied to evaluate the results under correct conditions.

In the following tables the values of K appear only for such thicknesses of the solution as have given points of equal intensities with the solvent. The other values of K for thicknesses which did not give points of equal intensity have been rejected. In the tables c, denotes concentration of the blue in terms of Fe_2O_3 per litre, D, the thickness of solution layer. Panchromatic and infra-red sensitised plates were used in obtaining the values in the visible and extreme red regions.

TABLE I.

Absorption in visible and red regions.

Name and compositon.	c.	D.	K.	λ in visible region only. Violet end.	Red end.
Aged Prussian blue $M/5 : M/5$.	0·05 g.	5 cm.	640·0	3693Å	5275Å
		6	533·3	3847	5198
		7	457·1	3924	5082
		10	320·0	4156	4812
		5	640 0	3809	5236
		6	533·3	3924	5198
Aged Turnbull's blue $M/5 : M/5$.	0·05 g.	7	457·1	4001	5082
		8	400·0	4079	5005
		9	355·5	4156	4967
		10	320·0	4195	4812

TABLE II.

Absorption in visible and extreme red regions.

Name and composition.	*c.*	*D.*	*K.*	Visible region.	Extreme red region.
Fresh Prussian blue *M*/5 : *M*/5.	0·005 g.	7·7cm.	4156	6935Å	7113Å
		10	3200	6742Å	?
Fresh Turnbull's blue *M*/5 : *M*/5.	0·005 g.	2·8	11428·5	?	6842Å
		3·6	8888·8	?	7112
		6·0	5333·3	6357Å	?
		7·7	4156	6202	?
		10	3200	5970	?
Aged Prussian blue *M*/5 : *M*/5.	0·005 g.	7·7	4156	6473Å	6957Å
		10	3200	6279Å	7228
Aged Turnbull's blue *M*/5 : *M*/5.	0·005 g.	7·7	4156	?	6687
		10	3200	6395Å	6995

TABLE III.

Absorption in ultraviolet region.

Name and composition.	*c.*	*D.*	*K.*	λ.
Aged Prussian blue *M*/5 : *M*/5.	0·005 g.	1·3 cm.	24615·4	2876Å
		2·8	11428·5	3130
		3·6	8888·8	3177
		4·6	6956·6	3379
		6·0	5333·3	3426
		7·7	4156	3459
Aged Turnbull's blue *M*/5 : *M*/5.	0·005 g.	1·0	32000	2613
		2·15	14885	2682
		2·8	11428·5	2815
		3·6	8888·8	2866
		4·6	6956·6	3059
		6·0	5333·3	3121
		7·7	4156	3229

TABLE IV.

Absorption in ultraviolet region.

Name and composition.	*c.*	*D.*	*K.*	λ.
Aged Prussian blue *M*/20 : *M*/20.	0·005 g.	1·3 cm.	2615·4	2759Å
		1·65	19394	2801
		2·8	11428·5	2932
		3·6	8888·8	3059
		4·6	6956·6	3177
		6·0	5333·3	3219
Aged Turnbull's blue *M*/20 :*M*/20.	0·005 g.	2·15	14885	2730
		2·8	11428·5	2824
		3·6	8888·8	2946
		4·6	6956	3060
		6·0	5333·3	3111
		10	3200	3248

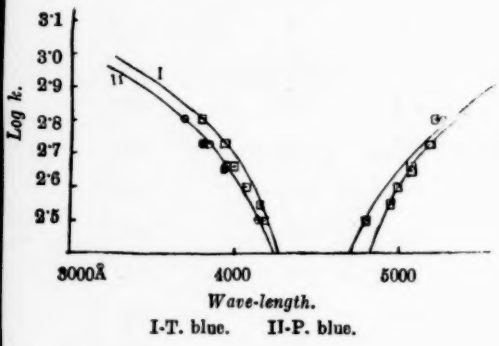
TABLE V.

Absorption in ultraviolet region.

Fresh Prussian blue *M*/5 :*M*/5.	0·005 g.	0·21 cm.	148850	2316Å
		0·36	88888	2373
		0·46	69566	2524
		0·60	53333	2660
		1·00	32000	2881
		2·15	14885	3050
Fresh Turnbull's blue *M*/5 :*M*/5.	0·005 g.	0·77	41560	2434
		1·00	32000	2528
		1·3	24615·4	2641
		1·65	19394	2716
		2·15	14885	2759

FIG. 1.

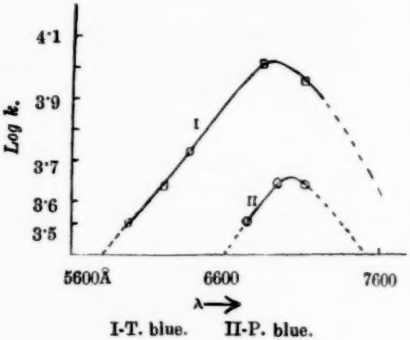
Absorption in visible region only for aged P. and T. blues (cf. Table I).



I-T. blue. II-P. blue.

FIG. 2.

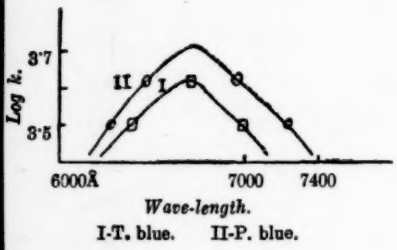
Absorption in visible and infra-red regions for fresh P. and T. blues (cf. Table II).



I-T. blue. II-P. blue.

FIG. 3.

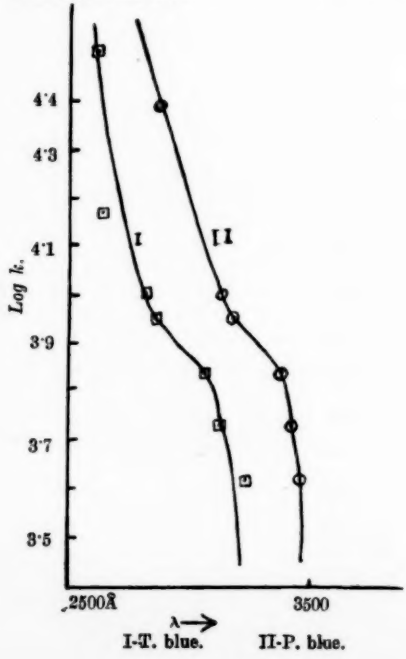
Absorption in visible and infra-red regions for aged P. and T. blues (cf. Table II).



I-T. blue. II-P. blue.

FIG. 4.

Absorption in ultraviolet for aged P. and T. blues (cf. Table III).



I-T. blue. II-P. blue.

FIG. 5.

Absorption in ultraviolet for aged P. and T. blues (cf. Table IV).

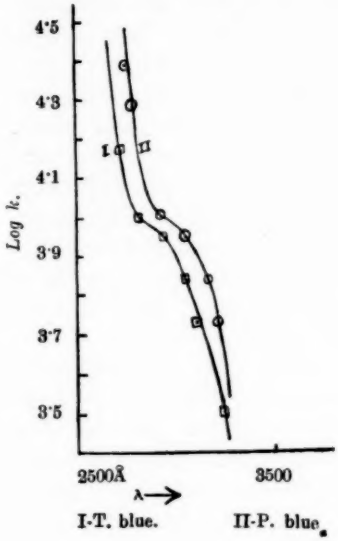
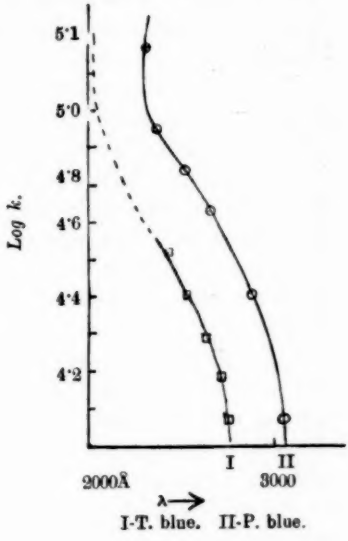


FIG. 6.

Absorption in ultraviolet for fresh P. and T. blues (cf. Table V).



DISCUSSION.

From the accompanying absorption curves the following observations seem to be striking and may be deemed to throw some light on the composition and constitution of Prussian and Turnbuli's blues:—

(*a*) The curves show that the absorptive power of Turnbull's blue is much greater than the Prussian blue when prepared fresh, and their absorptive power tends to be equal with the ageing of the preparations.

(*b*) That the shape of the absorption curves is quite similar, but for a little shift in the range of absorption.

(*c*) The absorption maxima appear in most of the solutions for the same values of K or in other words for the same thicknesses of the solution.

From the foregoing observations it becomes evident that the compositions of Prussian and Turnbull's blues tend to approach each other more closely when they are prepared by the ageing process than when fresh; and this is in close agreement with the results of chemical analysis already published (*Z. anorg. Chem.*, 1933, **213**, 240).

The shift of the absorption bands may be due to (*i*) the different proportion of Prussian and Turnbull's blues formed in course of the reaction between the reactants, iron and ferrocyanogen salts, and (*ii*) also due to the difference in the size of the particles of Prussian and Turnbull's blues when they are freshly precipitated. When the blues are prepared by ageing processes, both Prussian and Turnbull's blues seem to approach an average uniformity of size and composition in consequence of which their absorption curves approach each other closely.

As the shape of the absorption curve determines the constitution of a substance, it may be further suggested that the structural formulæ of these substances are similar to, if not identical with each other. The greater absorptive power of freshly prepared Turnbull's blue may be due to an excess of the ferrous molecules in which the ferrous iron is not saturated with regard to its maximum valency and therefore shows a greater absorption like many well-investigated organic compounds which, because of their unsaturated nature, show greater absorption than the saturated ones.

Summary.

1. Absorption spectra of a few preparations of Prussian and Turnbull's blues have been studied in the visible, infra-red, and ultra-violet regions and their compositions elucidated from their absorption curves.

2. The absorption curves of Prussian and Turnbull's blue prepared fresh are much farther apart from each other than those of the aged compounds, from which it has been inferred that on ageing, these compounds approach each other in their compositions and these observations are in conformity with the results of chemical analysis already published.

3. From the similarity in the shape of the absorption curves of Prussian and Turnbull's blues it has been suggested that their molecular structures are similar and the greater absorptive power of

Turnbull's blue when freshly prepared has been suggested to be due to an excess of ferrous molecules where the ferrous iron is not saturated with regard to its maximum valency.

I wish to thank Dr. N. R. Dhar of the Allahabad University for his kind interest and helpful suggestions in connection with the work. Thanks are due to Dr. R. Samuel of the Aligarh University for kindly allowing me to work in the Physics Laboratory there and for the guidance that he and his Assistant Dr. R. K. Asundi, whose help I gratefully acknowledge, have given me while taking the absorption photographs of the solutions. I thank my friend Mr. N. Ghatak for his kindly helping me to take a few photographs with constant deviation spectrograph at the chemistry laboratory of Allahabad University.

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Photochemical Reaction between Iodine and Oxalate.

BY N. R. DHAR, A. K. BHATTACHARYA AND B. L. MUKERJI.

Amongst the photochemical reactions taking place in solutions, the iodine-oxalate reaction is one which has been investigated by several chemists. Since 1916, when one of the authors (Dhar, *Proc. K. Akad. Wetensch. Amstardam*, 1916, **16**, 1097; *J. Chem. Soc.*, 1917, **111**, 707; 1923, **123**, 1856; *Anal. Chim.*, 1919, **9**, 130) showed that this reaction is highly sensitive to light and that the dark reaction is slow and has a very high temperature coefficient, a great deal of work has been carried on this chemical change. Unfortunately, there is disagreement in the results obtained by different workers (Berthoud and Bellenot, *Helv. Chim. Acta*, 1924, **7**, 307;

Berthoud, *Trans. Faraday Soc.*, 1931, **27**, 527; *Helv. Chim. Acta*, 1933, **16**, 393; Briers, Chapman and Walters, *J. Chem. Soc.*, 1926, 562; Mukherji and Dhar, *J. Phys. Chem.*, 1928, **32**, 1306; Bhattachary and Dhar, *J. Indian Chem. Soc.* 1929, **6**, 451, 473; 1930, **7**, 677; Dhar, Bhattacharya and Mukherji, *Nature*, 1933, **131**, 840; Young and Style, *Trans. Faraday Soc.*, 1931, **27**, 493; Allmand and Young, *ibid.*, p. 515; Griffith and McKeown, *ibid.*, 1932, **28**, 107, 752).

Dhar showed that the addition of an iodide markedly retards this as well as several other reactions involving iodine. Most of the researches on the kinetics of this reaction have been carried on with aqueous solutions of iodine dissolved in potassium iodide and hence the observed velocities have been greatly decreased by the presence of potassium iodide. In order to avoid the retarding influence of potassium iodide, we have carried on experiments with aqueous solutions of iodine without any potassium iodide and the results are recorded in this communication, which also contains an important relation between light absorption and chemical reactivity.

Experimental.

Merck's pure iodine was carefully sublimed for further purification. The potassium oxalate used was Merck's guaranteed reagent purified by recrystallisation from solutions in conductivity water. All solutions were prepared in conductivity water.

For the ultraviolet light source a Hanau quartz-mercury vapour lamp and for the infra-red, an 8000 watt gas-filled tungsten filament lamp were used. The solution filters used for the ultraviolet light have already been described (Bhattacharya, Prakash and Dhar, *Z. anorg. Chem.*, 1932, **209**, 139). For isolating radiations of wavelengths 8500Å, a saturated solution of potassium dichromate in a cobalt glass cell of 1 cm. thickness and for 8750Å, the same solution in a cobalt glass cell and *N*/7000-neocyanine in a 1 cm. thick glass cell were used. The reaction vessel was a quartz 3 cm. cube cell. For measurements of the energy absorbed a Moll thermopile with a sensitive galvanometer was used. The velocity of the reaction was followed by estimating the unchanged iodine against dilute solutions of sodium thiosulphate. The following experimental results have been obtained.

TABLE I.

N-$K_2C_2O_4$ and $N/850$-I_2, 20 c.c. of each solution mixed.

Condition.	Temp.	$K_{\frac{1}{2}}$ (semimolecular) after deducting the dark reaction.	Temp. Coeff.	Quantum yield.
Dark	15°	Unimol. K_1: 0·000310 (1)		
	20	0·000677 (2)	4·64 (1 + 3)	—
	25	0·00144 (3)	4·21 (2 + 4)	—
	30	0·00285 (4)		
	40	0·0116 (5)	4·07 (4 + 5)	—
3536Å (corning glass)	15	0·0153		98
	20	0·0253	2·44	216
	25	0·0374		342
3125Å	15	0·00168		—
	20	0·0270	2·38	
	25	0·0400		
3452Å	15	0·0168		83
	20	0·0270		228
	25	0·040	2·38	367
3512Å	15	0·0234	2·25	88
	20	0·0352		135
	25	0·0527		220
3340Å	15	0·0275	2·02	106
	20	0·0403		164
	25	0·0555		242
8500Å	20	0·00413	3·54	1·05
	25	0·00820		5·4
	30	0·0146	3·36	9·7
	40	0·0491		
8750Å	15	0·00143		
	20	0·00285	3·92	—
	25	0·00560		

It has been shown in a previous publication (*J. Phys. Chem.*, 1931, **35**, 2383) that a light filter consisting of K_2CrO_4 (0·03 g. in 100 c.c.) and $CoCl_2$ (saturated solution, 3·66M) each in a quartz cell of 1 cm. thickenss transmits radiations of mean wave-lengths 3125Å. Similarly 2·08M-nickel nitrate and 3·66M-$CoCl_2$ transmit 3452Å, 0·00154M-$K_2Cr_2O_7$ and 3·66M-$CoCl_2$ transmit 3512Å and 3·66M-$CoCl_2$ transmits 3340Å.

For obtaining radiations of mean wave-length 3536Å, a corning glass filter was used. The amount of light transmission by this filter

is much less than that of the solution filters and hence the velocity of the reaction is less than with other filters.

In this as well as in many exothermal photochemical reactions, the quantum yield is much greater than unity and increases markedly with the increase of temperature and the acceleration of the reaction by light absorption. It appears that the energy given out by the reaction is utilised in the activation of further molecules of the reacting substances and hence the quantum yield is greater than unity. In these exothermal photochemical reactions, the activation of the reacting molecules or their atomisation and the loosening of the binding forces of the molecules are produced by the absorbed light and the energy liberated in the chemical changes.

Relation between the Velocity of the Reaction and the Intensity of the Incident Radiation (or Absorbed Energy).

The majority of workers believe that the velocity of this reaction in light is not directly proportional to the intensity of the incident radiations but varies as the square root of the intensity of incident radiation, although A. K. Bhattacharya and N. R. Dhar have observed that by using an aqueous solution of iodine and in radiations of mean wave-lengths 5650Å, and 7304Å, the relation between the velocity and the light intensity approaches unity. The following results show that the relation between the velocity and incident light intensity in the reaction between N-$K_2C_2O_4$ and $N/850$-I_2 at 20° in absence of potassium iodide can vary from 1/3 to 5/4.

TABLE II.

Wave-length ...	3512Å	3340Å	3536Å (corning glass)	8500Å	8750Å
Observed ratio of velocities	1·32	1·79	3·25	3·97	2·71
Ratio of incident light intensity	4	4	6·25	4·34	2·44

The results recorded in Tables I and II show that when the photochemical reaction between potassium oxalate and aqueous iodine is highly accelerated by ultraviolet radiations, the velocity varies as $I^{\frac{1}{2}}$ except in the case of the corning glass filter, which transmits less than the solution filters, whilst in presence of infra-red radiations of wave-lengths 8750Å, which accelerate the reaction much less than ultraviolet light, the reaction velocity is proportional to $I^{\frac{1}{4}}$. With the

corning glass filter, the acceleration of the reaction was less than with the solution filters and the velocity is nearly proportional to $I^{\frac{1}{2}}$ with the corning glass. We have observed that the amount of light absorbed by the reacting mixture is directly proportional to the intensity of the incident radiation. Hence the reaction between potassium oxalate and aqueous iodine is not always proportional to the square root of the light intensity as assumed by Berthoud and Bellenot, Briers, Chapman and Walters, and Allmand and Young (*loc. cit.*), but can vary as $I^{\frac{1}{2}}$ to $I^{\frac{2}{3}}$ depending on the acceleration of the reaction in presence of light. This is certainly one of the many reactions which have been proved by us (Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 473; Dhar and Bhagwat, *Z. anorg. Chem.*, 1930, **190**, 415; *ibid.*, 1931, **199**, 406) to show a variable relation between the velocity and the light intensity or the amount of energy absorbed.

Temperature Coefficients.

From the results recorded in Table I, it will be seen that the temperature coefficient of the dark reaction velocity has the value 4·64 between 15° and 25° and 4·21 between 20° and 30°. The temperature coefficient in ultraviolet light, which markedly accelerates the reaction, varies from 2·02 to 2 44 between 15° and 25°. Moreover, it will be observed that the greater the velocity of the reaction in light, the smaller is the temperature coefficient of the reaction.

When the reaction is accelerated by infra-red radiations of wave-lengths 8500Å and 8750Å, which affect the velocity much less than ultraviolet, the difference between the temperature coefficients of the thermal and photochemical velocities is much less. In radiations of wave-lengths 8500Å, the temperature coefficient between 20° and 30° has the value 3·54 and in radiations of wave-lengths 8750Å, the value between 15° and 25° is 3·92. Hence we can conclude that the greater the acceleration of the reaction due to light absorption, the smaller is the temperature coefficient of the velocity or of quantum yield.

It has already been reported that iodide ions markedly retard this reaction. We have carried on some experiments on the dark reaction in presence of KI, because recently Berthoud reported that he could not reproduce our previous results nor the results obtained by himself

and Bellenot. We have obtained the following results in the dark with N-$K_2C_2O_4$ and $N/850$-I_2 containing $N/277$-KI; 20 c.c. of each solution were used.

TABLE III.

Temp.	K_1 (unimolecular).	Temp- Coeff.
22°	0·0000508	—
32°	0·000449	8·84
42°	0·00325	7·20

The Arrhenius A for this reaction has the very high value 18800. It will be interesting to note that the Arrhenius A for the velocity of the decomposition of an aqueous solution of trichloroacetic acid in the dark has also the high value 18610. Using $1·5N$-$K_2C_2O_4$, $0·0088N$-I_2 and $0·034N$-KI, Dhar obtained 7·2 as the value of the temperature coefficient for a 10° rise between 25° and 40° and the Arrhenius A = 18355. In the earlier experiments of Dhar, the amounts of the reacting substances were such as to make the velocity of the reaction in the dark a little higher than those recorded above. Hence the Arrhenius A is slightly smaller than the present value. The foregoing results show that when the reaction velocity is greatly retarded due to KI, the temperature coefficient of the dark reaction, which has the value 4·64 between 15° and 25° (Arrhenius A = 13160) in absence of KI, markedly increases and the results are entirely reproducible. It has been repeatedly observed in these laboratories that retardation of a reaction by a negative catalyst generally causes an increase in the temperature coefficient of the velocity of a reaction.

On applying the Perrin-Lewis radiation hypothesis, we get 8600Å as the maximum wave-length capable of accelerating the reaction in presence of KI and 10500Å for the reaction in the absence of potassium iodide. Actually we have been able to accelerate the reaction in absence of KI by radiations of wave-lengths 8500Å and 8750Å and the reaction in presence of KI by radiations of $\lambda = 8500$Å.

Influence of Stirring on the Kinetics of the Reaction.

Attempts have been made from time to time to determine whether the velocity of a homogeneous photochemical reaction is affected by shaking or stirring the reacting substances. Recently Young and Style (*loc. cit.*) have shown that the temperature coefficient of the

photochemical reaction between potassium oxalate and iodine in presence of KI markedly decreases when the mixture is well stirred. From the laws of light absorption, Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1932, **9**, 535) have deduced a relation, which shows that when the relation between the light absorption and the velocity of the reaction deviates markedly from unity, stirring will lead to increased velocity and decreased temperature coefficient. As this is an interesting point, we have carried on some measurements on the influence of stirring on this reaction. The reacting substances were placed in the same reaction vessel as before and stirred by a stout glass rod driven by a small motor. The amount of light falling on the mixture in these experiments is less than in the previous experiments as the light was allowed to pass through an aperture of a diaphragm with a diameter 2·5 cm. The results are as follows with 10 c. c. of N-$K_2C_2O_4$ and 10 c.c. of $N/850$-aqueous iodine without KI.

TABLE IV.

Wave-length.		Temp.	$K_{\frac{1}{2}}$ (semimolecular) after deducting the dark reaction.	Temp. Coeff.
8500Å.	Stirred	20°	0·0459	1·62
		30	0·0745	
	Unstirred	20	0·00361	3·5
		30	0·01263	
3340Å	Stirred	20	0·0736	1·42
		30	0·1044	
	Unstirred	20	0·0400	2·02
		30	0 0804	
3536Å (corning glass)	Stirred	20	0·0520	1·51
		30	0·0786	
	Unstirred	20	0·0224	2·40
		30	0·0537	

The foregoing results show that on stirring, the velocities of the reaction in radiations of wave-lengths 3340, 3536 and 8500Å are greatly increased and the temperature coefficients are considerably

lowered. Moreover, the temperature coefficients in the stirred reaction mixtures show much less variation in radiations of different wave-lengths than in the unstirred condition.

In this reaction, the light absorption is high and the reaction is markedly accelerated by stirring. When the light absorption is feeble, stirring is not likely to influence the velocity.

It has already been reported that in radiations of wave-lengths 8500Å when the light intensity is varied, the observed ratio of velocities has the value 3·97 when the ratio of the light intensity is 4·34. We have investigated the influence of stirring on the relations between the velocity and the light intensity in radiation of wave-lengths 8500Å and the experimental results at 20° are recorded below.

TABLE V.

N-$K_2C_2O_4$ and $N/850$-iodine (10 c.c. each).

Diameter of the aperture.	$K_{\frac{1}{2}}$ (semimolecular) after deducting the dark reaction.	Ratio of velocities.	Ratio of light intensity.
2·5 cm.	0·0459 (I)	$\frac{I}{II}=1·51$	4·34
1·2	0·0303 (II)	$\frac{II}{III}=1·09$	1·40
1·0	0·0277 (III)	$\frac{I}{III}=1·66$	6·25

These results show that when the solution is stirred, the velocity of the reaction between potassium oxalate and aqueous iodine in radiations of wave-lengths 8500Å is greatly increased and it becomes nearly proportional to $I^{\frac{1}{2}}$, whilst with the unstirred solution the reaction is nearly directly proportional to the light intensity in radiations of wave-lengths 8500Å. It is of interest to note that in the dark reaction in presence of an excess of potassium oxalate, the rate of disappearance of iodine follows the unimolecular formula but in presence of ultraviolet, visible or infra-red radiations, the velocity of the disappearence of iodine, is semimolecular. This behaviour is also observed with some other photochemical reactions involving iodine, *e.g.*, sodium formate and iodine; sodium citrate and iodine; sodium malate and iodine; ferrous sulphate and iodine ; and sodium nitrite and iodine.

It is difficult to state whether this behaviour is an absorption effect only or due to the formation of atomic iodine on illumination.

Chemical Reactivity and Light Absorption.

From the researches of Pringsheim and Rosen (*Z. Physik*, 1928, **50**, 1) we know that there are four absorption spectra of iodine; the well known red-green absorption, two absorption spectra in the ultraviolet below $\lambda=2000$Å and a very faint one in the infra-red (>8000Å). This latter is likely to belong to a metastable level. The acceleration of the iodine-oxalate reaction in radiations $\lambda=8500$Å and 8750Å as actually observed may be due to this metastable level.

We have carefully measured the extinction coefficients of a mixture of N-$K_2C_2O_4$ and $N/850$-aqueous iodine by a Nutting's spectrophotometer and the results are given below.

TABLE VI.

Wave-length (Å) ...	7000	6707	5970	5670	5490	5320	5200	5000
Extinction coeff. ...	0·03	0·06	0.10	0·14	0·18	0·20	0·24	0·28
Wave-length (Å) ...	4910	4800	4720	4670	4550	4400		
Extinction coeff. ...	0·32	0·36	0·41	0·46	0·51	0·60		

These results show that all radiations between 7000 to 4400Å are absorbed by aqueous iodine.

From the results recorded in the foregoing pages, it will be seen that the iodine-oxalate reaction is markedly accelerated by infra-red radiations of wave-lengths 8500Å and 8750Å. The limits of sensitised decomposition and photochemical decomposition with iodine molecules are 8050Å and 4995Å respectively. It appears, therefore, that the presence of oxalate markedly sensitises the decomposition of iodine molecules, which become reactive in radiations of longer wave-lengths on the addition of oxalate. Using a copper arc we have carefully photographed the absorption spectra of $N/1700$-aqueous iodine and $N/2$-potassium oxalate separately and a mixture containing 10 c.c. of N-$K_2C_2O_4$ and 10 c.c. of $N/850$-aqueous iodine and we find that the iodine solution alone shows almost complete absorption in the ultraviolet from 2700Å, whilst with the oxalate solution, almost complete absorption in the ultraviolet begins from 3000Å. In the case of the mixture of the iodine and oxalate, almost complete absorption in the ultraviolet starts nearly from 3826Å. These results showing that the absorption of light by a solution of an oxalate is appreciably increased by the addition of a dilute iodine solution, are of great interest from the view point of the nature of chemical reactivity. In other words,

the sensitisation of an oxalate solution by iodine is associated with marked increase of light absorption in the ultraviolet.

In the reaction between oxalate-iodine, the chemical change involved appears to be

$$C_2O_4'' + I_2 = 2CO_2 + 2I'.$$

Similar is the case with the other halogens with oxalic acid or an oxalate. That oxalate ion is taking part in these reactions is evident from the fact that the velocity of reaction is greater with an oxalate than oxalic acid. The first stage in these reactions appears to be the formation of an additive compound of the halogen molecule and the reducing agent having greater light absorption capacity and not the atomisation of the halogen molecules as has been hitherto supposed.

SUMMARY.

1. The reaction between an excess of potassium oxalate and aqueous iodine in absence of KI is unimolecular in the dark and semi-molecular in light.

2. The temperature coefficient of the reaction velocity between 15° and 25° has the values 4·64 (dark), 3·92 (8750Å), 3·54 (8500Å), 2·44 (corning glass 3536Å), 2·38 (3452Å), 2·38 (3125Å), 2·25 (3512Å), 2·02 (3340Å). The greater the acceleration due to light, the smaller is the temperature coefficient. The velocity of the reaction is greatly retarded by KI and in its presence ($N/277$), the temperature coefficient between 22° and 32° in the dark has the value 8·84.

3. The relation between the velocity and the incident light intensity or the absorbed energy is not constant but varies from 1/3 to 5/4. When the reaction is much accelerated by light the relation becomes small and when the acceleration due to light is comparatively small, the relation has a higher value.

4. When the reaction mixture is stirred, the reaction velocity in light is markedly accelerated and the temperature coefficient is lowered.

5. Almost complete absorption of light in the ultraviolet by a normal solution of an oxalate begins from 3000Å, by a $N/850$ solution of iodine from 2700Å, whilst with the mixture of oxalate and iodine almost complete light absorption begins from 3826Å. Hence the absorption of light by a solution of an oxalate is appreciably increased by the addition of iodine.

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The Dissociation Constant of Eugenol.

By Gadiyara Gundu Rao.

Lunden (*Z. physikal. Chem.*, 1910, **70**, 249) has determined the dissociation constants of phenols by measuring the hydrolysis of their salts. He pointed out that very accurate results can be attained only if the salt of the phenol undergoes a large hydrolysis. Consequently he recommends the investigation of the ammonium salt instead of sodium or potassium salt. In the case of eugenol the same method can be applied; only eugenol being difficultly soluble in ammonia caustic soda had to be used.

Assuming that sodium eugenate and hydroxide dissociate completely and eugenol does not at all dissociate, which is only approximately true, we can write

$$X=\frac{K_v-K_s}{K_{OH}-K_a}$$

where X is the fraction of eugenate hydrolysed and K_v, K_s and K_{OH} represent respectively the equivalent conductivity of the solution of sodium eugenate at the dilution of V litres, that of the salt solution with the hydrolysis suppressed and of sodium hydroxide solution. K_s is determined after suppressing the hydrolysis by the addition of an excess of eugenol. X, the degree of hydrolysis being found, the hydrolysis constant K_h is evaluated by the relation,

$$K_h=\frac{X^2}{(1-X)\,V},$$

V being the dilution. Then the dissociation constant K_a is related to the dissociation constant of water K_w by the relation,

$$K_a=\frac{K_w}{K_h}.$$

Experimental.

A sample of eugenol was distilled after drying over anhydrous magnesium sulphate. The distillation was repeated until the distillate was almost colourless. This was considered pure since its refractive index was the same when purified by acetylation and subsequent hydrolysis with alkali.

The caustic soda employed was prepared from metallic sodium and during the preparation care was taken to exclude atmospheric carbon dioxide. It was diluted with gas-free, conductivity water and preserved free from atmospheric carbon dioxide. The solution was standardised by weight with pure oxalic acid.

The solutions of sodium eugenate were made in every experiment by mixing equivalent amounts of sodium hydroxide solution and freshly distilled eugenol. The hydrolysis in these solutions was suppressed when required by the addition of a few drops of eugenol.

The conductivity vessel employed had two platinum electrodes of 1 cm. diameter and about 2·5 cm. apart and was provided with a thermometer stopper.

While carrying out an experiment a definite weight of the standard alkali was treated with an exactly equivalent amount of eugenol. This solution was diluted to the required concentration by the addition of weighed quantity of freshly distilled water. A small amount of this solution was transferred into the cell and its conductivity determined. Excess of eugenol was shaken with the remaining solution for sometime and the conductivity of that solution was also similarly determined.

It was found that eugenol does not readily dissolve in weak alkali and, therefore, always a strong solution of alkali was treated with eugenol and the solution was diluted afterwards. The low solubility of eugenol is an obstacle to the complete and quick suppression of hydrolysis, especially when the solution is dilute. Therefore higher dilutions than 50 litres were not tried.

In the following table the results of a series of experiments all conducted at 25° are given. V denotes the dilution in litres. K_v and K_∞, the equivalent conductivity of hydrolysed and unhydrolysed salt solutions respectively ; a, the percentage of hydrolysis ; K_A, the

hydrolysis constant ; K_a, the dissociation constant of eugenol. For the water constant K_w, Kohlrausch's value $1{\cdot}11 \times 10^{-14}$ is taken.

Expt.	V.	K_v.	K_s.	a.	$K_h \times 10^4$.	$K_a \times 10^{10}$.
1	9·49	63·51	57·18	3·4	1·24	0·89
2	13·69	67·61	61·45	3·4	0·86	1·30
3	13·69	67·42	61·90	3·0	0·69	1·62
4	14·80	67·11	60·49	3·6	0·91	1·23
5	14·92	66·85	59·05	4·2	1·24	0·90
6	17·37	70·20	63·46	3·7	0·83	1·34
7	17·46	70·11	63·37	3·7	0·82	1·35
8	24·82	73·30	65·19	4·6	0·86	1·29
9	24·87	73 05	65·33	4·3	0·78	1·43
10	24·97	73·37	65·19	4·8	0·98	1·13
11	25·00	73·10	65·06	4 5	0·84	1·32
12	46·34	79 34	67 69	6·6	1·00	1·11
13	46·58	79·09	67·44	6·6	0·99	1·12
14	47 06	79·75	67·84	6·8	1·03	1 97
15	47·58	80·83	68·74	6·9	1·36	1·04
16	47·60	80·15	68·34	6·9	1·01	1·10
17	47·84	80·46	68·92	6·6	0·97	1·15

Conclusion.

In the above solutions it is only an approximation to assume complete dissociation of the sodium eugenate as they are still not sufficiently dilute. The progressive increase in K_s with dilution shows that dissociation of the salt is not quite complete even at 50 litres dilution. This is responsible for the change in the value of K_h and K_a noticed with changing dilution.

The above values for K_a, however, can give us an idea of the strength of eugenol as an acid. The dissociation constant is of the order of 1×10^{-10} and therefore eugenol is about as acidic as phenol itself. Regarding the actual value of the dissociation constant, its determination is accurate only at very high dilutions.

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Adsorption Indicator in the Volumetric Estimation of Sulphates. A Colloido-chemical Study.

By M. P. Venkatarama Iyer.

Wellings has pointed out in a paper (*Trans. Faraday Soc.*, 1932, **28**,561) the applicability of fluorescein (evidently sodium fluorescinate) as an adsorption indicator in the volumetric estimation of soluble sulphates. He has offered a tentative explanation for the colour changes which the precipitate at the end-point undergoes, when magnesium or manganese sulphate solution is titrated against barium hydroxide using the adsorption indicator. It is clear from the 'probable' explanation offered by him in the above mentioned paper that the mechanism of the reactions at the interface has not been fully elucidated. "The anions of the fluorescein are not adsorbed by the colloidal particles of the metallic hydroxide so long as the sulphate ions are present in excess. When, however, the sulphate ions are removed as barium sulphate, the fluorescein anions are then adsorbed and change colour as soon as barium ions are also adsorbed. The colour change is, therefore, visible when there is a drop of barium hydroxide solution in excess." The object of the present communication is to elucidate the exact mechanism of the changes taking place in the system. The phenomena connected with the colour changes in the system, the influence of p_H changes in the reaction mixture, and of the ion environment during the course of the titration, have also been elucidated from the colloido-chemical standpoint.

In order to show that the magnesium hydroxide and not the barium sulphate gives rise to the colour change at the end-point of the titration, the following experiments were tried. In a stoppered bottle containing magnesium hydroxide, freshly precipitated from magnesium sulphate and sodium hydroxide solution (the precipitate being thoroughly washed free from soluble sulphate), a few drops of sodium fluorescinate were added and shaken up with water. After allowing to stand, the precipitate was coloured pink, showing the same colour as

that obtained in the titration of magnesium sulphate against barium hydroxide. The colour change was marked in the case where the magnesium hydroxide was precipitated with a slight excess of magnesium salt; and not so well where a slight excess of alkali was used for the preparation.

The colour changes with fluorescinate as indicator, take place when solutions of manganese or magnesium sulphates are titrated against barium hydroxide and do not take place in the titration of other soluble sulphates. From the table of the precipitation of p_H of the hydroxides of metals (Britton, "Hydrogen Ions," 1932, p. 325) it is found that for Mg it is 10·5, and for Mn, 8·5—8·8, while for other metals such as Cu, Al, Fe, Zn, etc., the precipitation p_H is in the acid range. Thus the success of the experiment using Mg and Mn sulphates can be attributed to the precipitation p_H of these hydroxides being in the distinctly alkaline range. The p_H at the equivalence point should be in the alkaline range in order that there may be a sufficient concentration of fluorescinate ions which can be adsorbed. The adsorption of fluorescinate ions by the surface will depend upon other factors such as the electrical charge of the surface, as also the presence or otherwise of other strongly adsorbable ions namely the hydrogen and hydroxyl ions or the constituent ions of the solid phase (*cf.* Mukherjee and Iyer, *J. Indian Chem. Soc.*, 1926, **3**, 307). The above considerations can easily explain why the colour change does not take place when aluminium sulphate is titrated against barium hydroxide. It is seen that since the precipitation p_H of aluminium hydroxide is in the neighbourhood of 4·0, the precipitate can adsorb on its surface either hydrogen ions or aluminium ions or both, when the p_H corresponds to this value.

The process of adsorption taking place on the surface of magnesium hydroxide particles, when magnesium sulphate is being titrated against barium hydroxide, may be pictured as follows. The precipitate during the initial stage of the titration and until the end-point is reached adsorbs 'primarily' on its surface a layer of magnesium ions, since this is the constituent ion of the solid phase; the mobile sheet of the double layer consisting of sulphate or hydroxyl ions. The 'electrical' adsorption of fluorescinate ions in the 'mobile' layer, or the 'deforming' influence by the primarily adsorbed magnesium ions on the fluorescinate ions will depend upon the nature and concentration of other ions in solution which are likely to be adsorbed by the hydroxide. The colour change taking place on the

precipitate is due to this 'deforming' influence on the dyestuff anions as has been pointed out by Fajans (*Z. Elektrochem.*, 1923, **29**, 495 ; *Z. anorg. Chem.*, 1924, **137**, 221).

The above considerations are illustrated by the following experiments. A series of bottles containing the same volume (10 c.c.) of 0·1*N*-magnesium sulphate solution were shaken up with 5 drops of sodium fluorescinate solution (0·5 % strong) with varying volumes of barium hydroxide (0·1 *N*) in the neighbourhood of the equivalence point *viz.*, 9·5 c.c. to 10·5 c.c. On allowing the precipitates to settle for the same period (about 5 minutes) it was observed that there was the maximum intensity of pink colour in the precipitate when the solutions were mixed up in exactly equivalent proportions. The supernatant liquid in this case was practically colourless. On either side of the equivalence point the intensity of the yellow colour of the supernatant liquid (due to sodium fluorescinate) goes on increasing. The colour change of the precipitate is not anything so sharp as stated by Wellings. The equivalence point can be rather judged better by the intensity of the yellow colour of the solution after allowing the precipitate to settle, though this is rather tedious in routine titrations on account of the time taken by the precipitate to settle down. That the colour change of the precipitate is a gradual process is to be expected from the general principles relating to the adsorption by a precipitate in an enviornment consisting of ions of varying concentration and adsorbability. Beyond the equivalence point of the titration, the precipitate of magnesium hydroxide is in contact with a solution whose p_H is higher than 10·5 (the precipitation p_H of magnesium hydroxide) and as such shows strong preferential adsorption for hydroxyl ions. A distinct change in the colour of the precipitate from pink to light orange, is therefore, noticed owing to the desorption of the fluorescinate ions.

Another interesting observation made during the course of these experiments is that when the precipitate, at the equivalence point, which is coloured pink, is kept in contact with the titrated solution for a few hours (not more than 24 hours), a gradual fading in the colour of the precipitate takes place, while the yellow colour of the solution deepens. This shows that the effect of 'ageing' of the magnesium hydroxide particles, brings about a growth in size of the particles with a desorption of the 'primarily' adsorbed magnesium ions, and a corresponding number of fluorescinate ions in the 'mobile' layer. A feeble pink colour of the precipitate persists whatever be the length

of time for which it is kept, thus showing that the primarily adsorbed magnesium ions are responsible for the colour changes. Since the colour change is thus essentially due to the 'electrical' adsorption (according to Mukherjee's theory, *loc. cit.*) of the fluorescinate ions by the magnesium hydroxide, the effect of neutral salts like potassium chloride, potassium nitrate on the course of the titration has also been investigated. As Wellings has stated, the end-point is affected by the presence of these salts, though it has not been possible to make quantitative measurements of the change in the 'end-point' due to the presence of these salts. The end-point of the titration becomes very indistinct, because the simultaneous 'electrical' adsorption of the anions of the neutral salt as also of the fluorescinate ions becomes possible, the relative amounts so adsorbed being governed by their respective concentrations and adsorbabilities. Hence the colour change of the precipitate becomes indistinct. Hydroxyl ions, however, have a sharp effect on the end-point, on account of their strong adsorption by the surface of magnesium hydroxide.

Summary.

1. The work of Wellings on the titration of magnesium and manganese sulphates against barium hydroxide using fluorescein as adsorption indicator has been extended. The influence of the p_H of the solution and the ion environment has been pointed out.

2. The results have been explained on the basis of the 'chemical' and 'electrical' adsorption of ions by particles as put forward by Mukherjee, combined with theory of 'deformation' of ions at interfaces enunciated by Fajans.

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The Chemistry of Jute-lignin. Part VI. Isolated Lignin and Lignin Native in Jute.

By Pulin Behari Sarkar.

It is well known that isolated lignin is different from raw lignin as regards many colour reactions. Lignin separated from jute in the usual way has a dark appearance, although jute itself is practically white. It is for this reason, that according to the varying methods of isolation, different investigators have reported different types of lignins even when the source is the same.

Wood and similar lignified materials afford acetic acid when distilled with dilute mineral acids but lignin, prepared from these raw materials, does not give any trace of the aforesaid acid, when similarly treated. Jute also has been found to behave in a similar manner and lignin prepared from it does not give any acetic acid. Delignified jute and raw jute itself have been found to give the same amount of acetic acid (*cf.* Table I).

This fact leads to the conclusion that lignin native in jute does not contain any acetyl group as is held by Heuser (*Paper Trade J.*, 1930, **83**, 75). The view of Jonas (*Papier Fabrikant.*, 1928, **26**, 221) that the acetyl group is split off from lignin during isolation, is not justified. The acetic acid in delignified jute has been found to be due to the pectin residue as when all the pectin was extracted with 0·5% solution of ammonium oxalate at 80°-90°, the residue no longer gave any acetic acid. This also proves that cellulose or hemicelluloses are incapable of giving acetic acid under these circumstances. That pectin gives acetic acid has been shown by several investigators (Fuchs, "Chemie des Lignins", 1926, p. 234) and our results further corroborate their observations.

Like other lignins jute-lignin contains methoxy groups. Delignified jute has been found to give methoxy from which it may be concluded that pectin residue also contains methoxy group. It has been found that half of this methoxy residue in pectin is in the form of an ester, as the methoxy figure of delignified jute after boiling with 1% KOH is half that of the untreated sample (*cf.* Table II).

HCl-lignin has been shown before by the author (*J. Indian Chem. Soc.*, 1931, **8**, 397) to give CO_2 when boiled with 12% HCl but no furfural. The latter fact shows that no uronic acid or pectin residue is attached to lignin. Chloro-lignin from jute and separated lignin have now been found after repeated purification from acetone and alcohol to give CO_2 even in an atmosphere of hydrogen. This suggests the presence of COOH group in lignin with a negative group in the α-position, for it is well known that such organic compounds yield CO_2 more or less readily even when boiled alone or with mineral acids. This view of the presence of COOH is supported by Rassow and Wagner (*Wochenblatt f. Papier-fabrikation*, 1932, **63**, 103), who from the conductivity of Na-lignin from pinewood found the presence of three COOH groups, as also by Mehta (*Biochem. J.*, 1925, **19**, 961) who determined the acid value as 477.

Determination of CO_2 was done in raw jute, delignified jute and lignin respectively in order to find out any difference in its value and also to justify the presence of CO_2 residue in lignin (*cf.* Table III).

An attempt to get an idea of the formaldehyde content of lignin, native in jute, proved futile as no suitable method was found which could be relied upon in presence of furfural.

As has already been shown by the author (*J. Indian Chem. Soc.*, 1934, **11**, 691), the slight discrepancy in furfural value in raw and delignified jute is due to the liberation of formaldehyde from lignin. This indirectly proves that lignin should give no furfural which has actually been found to be the case with separated jute-lignin. Hence, separated lignin is identical with the native one in this respect.

Experimental.

Determination of acetic acid in raw and delignified jute.—1-1·5 G. of the sample (of known moisture content) was boiled under reflux with 100 c.c. of KOH solution for 3-4 hours. It was filtered, washed neutral and acidified with sulphuric acid. The precipitate was filtered off and the filtrate distilled in steam; this was continued until the distillate was neutral to litmus. Acetic acid was then estimated with $N/10$-alkali in the usual way. Blank experiments were done side by side to make a correction for sulphuric acid, which gives a little sulphurous acid on prolonged steam

distillation. 10% is the minimum strength of KOH that hydrolyses completely the acetyl group.

TABLE I.

Substance taken.	Hydrolysing agent and its strength.	Acetic acid (on dry sample).
Raw jute washed with neutral soap and made free from fat	0·5% KOH	5·89%
	1	5·82
	5	5·97
	* 10	6·29
	15	6·23
	20	6·26
	17·5% in the cold	4·73
	10% H_2SO_4	4·93
Delignified jute	10% KOH	7·53
	15	7·42
	20	7·73

As jute contains 15·43% of lignin, 84·57 g. of delignified jute, therefore, give 6·26 g. of acetic acid ; hence 100 g. of it would give 7·40 g. Actually 7·54 g. have been obtained from jute delignified by ClO_2 which, therefore, shows, the absence of acetyl group in lignin. Boiling of raw jute with 1% KOH for one hour for facilitating delignification was avoided for obvious reasons.

Presence of methoxy group in lignin and delignified jute and its determination.—In Zeisel's apparatus (with Perkin's modification) dimethylaniline was taken in the conical flask instead of usual alcoholic silver nitrate, other arrangements for methoxy determination remaining the same. The vapour of alkyl iodide at once formed crystalline derivatives. It was filtered, washed with $CHCl_3$ (in which it was but slightly soluble) and dried. It did not melt but decomposed at 220°, as also the fraction recovered from $CHCl_3$. The methoxy values were estimated in the usual way by Zeisel's method and the results are given in the following table.

TABLE II.

Sample.	Wt.	Moisture.	AgI.	Methoxy. (on dry sample).	Mean.
Raw jute	0·4102 g.	10·0 %	0·1127 g.	3·98 %	3·965
	0·5778	,,	0·1575	3·95	
Delignified jute (without alkali boiling)	0·6085	9·50	0·5598	1·318	1·338
	0·7162	,,	0·6673	1·358	
Do (alkali boiled)	0·6220	9·61	0·0260	0·601	0·608
	0·7685	,,	0·0325	0·616	
HCl-lignin (at room temp.)	0·3050	Nil	0·3787	16·38	16·41
	0·2806	,,	0·3496	16·44	

Jute contains 15·43% lignin (by HCl method) calculated on the dry sample, and if X be its actual methoxy content, then $15{\cdot}43\ X/100 + (100-15{\cdot}43) \times 1{\cdot}338/100 = 3{\cdot}965$, whence $X = 18{\cdot}37$. The methoxy value of separated lignin being 16·41%, it appears that lignin has suffered a loss of 1·96 % of methoxy in the course of isolation. It may be pointed out here that with a mol. wt. of 330, and 5 methoxy groups, the value comes to 18·66 %. This value of the mol. wt. of lignin has been arrived at by the author by the chlorination of lignin (*J. Indian Chem. Soc.*, 1934, **11**, 777) and by the determination of its formaldehyde content (*ibid.*, p. 691).

Determination of CO_2 *in jute, delignified jute and lignin.*—1 G. of the sample was boiled with 100 c.c of 12% HCl on a glycerine-bath and the gas was passed with CO_2-free air through an upright condenser to two gas-washers, each containing 100 c.c. of *N*/10-baryta for 4-5 hours. The supernatant liquid (25 c.c) was titrated next day with *N*/10-HCl and CO_2 was calculated in the usual way. The results are shown in the following table.

TABLE III.

Sample.	Wt.	Moisture.	*N*/10-baryta consumed.	CO_2 (on dry sample).	Mean.
Raw jute	1·2435 g.	10·2 %	8·75 c.c.	1·86 %	1·830
	1·1522	,,	9·15	1·80	
Delignified jute	1·1986	9·8	9·35	1·91	1·915
	1·2225	,,	9·65	1·92	
HCl-lignin (at room temp.)	1·5490	Nil	10·85	1·54	1·56
	1·8205	,,	13·10	1·58	

(100—15·43) *i.e.*, 84·57 g. of delignified jute would give 1·62 g. of CO_2, whence in raw jute the deficiency due to lignin is (1·830−1·62) *i.e.*, 0·21 g. Lignin, therefore, should give 1·38% of CO_2, while actually 1·56 % have been found. This value may not represent the theoretical one, for the splitting off of CO_2 is not usually quantitative in such cases. The moisture in the above experiments was determined by heating the sample under vacuum over P_2O_5 at 110° until the weight was constant.

Summary.

(1) It has been shown by an indirect method that lignin contains no acetyl groups. Isolated lignin in this respet is not different from the lignin native in jute.

(2) The absence of alkoxyl groups other than methoxy in jute-lignin has been definitely established.

(3) Lignin suffers a loss of 1·96 % of methoxy during isolation by HCl in the ordinary way. The theoretical value 18·37 % agrees fairly well with the assumption that lignin has a mol. wt. of 830 and has 5 methoxy groups.

(4) The CO_2 values of raw and delignified jute indicate that lignin should give CO_2; the calculated and actual values are almost coincident.

(5) Owing to difficulties in estimation, it is not possible to say how much H·CHO lignin native in jute should give.

In conclusion, it gives me much pleasure to record here my sincere and grateful thanks to Prof. J. C. Ghosh and Dr. J. K. Chowdhury for their kind interest and valuable suggestions.

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A Note on the Photochemical Reaction between Ethylene Iodide and Iodine in Carbon Tetrachloride Solution.

By D. S. Narayanmurti.

Schumacher and Wiig (*Z. physikal. Chem.*, 1930, **B, 11,** 45) represent the course of the above reactions as follows:

$$I_2 + h\nu \rightarrow I + I \quad \ldots (k_1) \quad \ldots (i)$$

$$I + C_2H_4I_2 \rightarrow C_2H_4I + I_2 \quad \ldots (k_2) \quad \ldots (ii)$$

$$C_2H_4I \rightleftharpoons C_2H_4 + I \quad \ldots (k_3) \quad \ldots (iii)$$

$$I + I \rightarrow I_2 \quad \ldots (k_4) \quad \ldots (iv)$$

and draw some interesting conclusions therefrom.

The decomposition of ethylene iodide should thus proceed from collisions between iodine atoms and ethylene iodide molecules. Now if the mechanism of reaction (*iv*) is ascertained, the total number of collisions between reacting bodies may easily be calculated. From a comparison of the total number of collisions with the number of effective collisions yielded by a study of the reaction kinetics, one is in a position to estimate the energy of activation (E). A second measure of E is given by the variation of the velocity of appearance of iodine (K) with temperature, for, this would be the only process involving activation by collision. Any agreement between the two values of E would give striking confirmation not only of the decomposition scheme assumed by Schumacher and Wiig, but also of the mechanism postulated for the union of the atoms of iodine.

From an inspection of the reaction scheme it is obvious that the velocity constant (K) for the formation of iodine is given by

$$K = k_2 \sqrt{\frac{2I_{abs}}{k_4}} \cdot [C_2H_4I_2]$$

where I_{abs} represents the energy absorbed by the reaction system per second per c.c. Of these quantities, K and I_{abs} are experimentally determinable and k_2 is known when a suitable value has been assigned to k_4. The value of k_4 depends solely on the mechanism assumed for reaction (*iv*). Alternatively k_2 may be estimated from a consider-

ation of the collision-frequency and a knowledge of the heat of activation (E).

Schumacher and Wiig postulate that one in every five collisions between iodine atoms in the presence of a solvent molecule, results in the formation of a molecule of iodine and deduce a value for k_2 which is 32 times of that arrived at from considerations of the temperature coefficient data. This low efficiency factor 1/32 for collisions between iodine atoms and ethylene iodide molecules is traced to the probable high steric factor, which the complexity of the iodide molecule is likely to bring to play.

While this argument is not wholly convincing, we have been led in our studies on the photosensitising action of iodine (*Z. physikal. Chem.*, 1934, **B, 26**, 255) to assume an efficiency of unity for the collisions of iodine atoms in the presence of a solvent molecule. We have, therefore, in the following examined the data of Schumacher and Wiig in the light of our data and found that the concept of a steric factor may completely be dispensed with in such reactions.

On this basis, we proceed to calculate Z_1, the total number of collisions between iodine atoms and iodide molecules and by comparing this number with the number Z_2, which represents the number of such collisions resulting in reaction, we obtain E. Thus

$$Z_2/Z_1 = e^{-E/RT}$$

Now Z_1 is given by the expression,

$$2\sqrt{2\pi}.a^2.\sqrt{RT}.\sqrt{\frac{M_1+M_2}{M_1M_2}}.n.n_e$$

where n is the number of iodine atoms per c.c., n_e, the number of iodide molecules per c.c., M, the mass of iodine atom, M_e, the mass of the iodide molecule, T, the temperature of the reaction, and a, the distance of nearest approach for reaction, of the centres of the iodide molecules and iodine atoms.

In this expression M, M_e, N_e and T are known. a is presumably equal to $\frac{1}{2}(S+S_1)$, where S and S_1 represent the diameters of the iodine atoms and iodide molecules respectively. $S = 2{\cdot}72 \times 10^{-6}$ cm. (Landolt, "Tabellen," Part I, p. 38). Unfortunately S_1 is not known so definitely: but in such cases not much error is introduced by assuming a round figure of 5×10^{-8} cm. ("The Kinetics of Reactions in Solutions," p. 15). Thus, $a = 4{\cdot}0 \times 10^{-8}$ cm. The only unknown then is n. This quantity may be determined as follows.

The number of iodine atoms per c.c. at the stationary state.— On the basis that every binary collision of iodine atoms in the presence of a solvent molecule results in the formation of a molecule of iodine, the number of iodine molecules (N) appearing in unit volume in unit time is equal to

$$k_4[I]^2 . \frac{k'N_s}{1/\tau + k'N_s}$$

where N_s is the number of molecules per c.c. of the solvent and τ, the life-period of the iodine atom. Since the magnitude of N_s is so much greater than that of $1/\tau$, the fraction $\frac{k'N_s}{1/\tau + k'N_s}$ reduces to unity; and

$$N = k_4[I]^2$$

and $[I]$ at the stationary state is given by $\sqrt{\frac{2I_{abs}}{h\nu . k_4}}$. Thus

$$N = k_4[I]^2 = k_4 \left[\sqrt{\frac{2I_{abs}}{h\nu . k_4}} \right]^2 = \frac{2I_{abs}}{h\nu}.$$

Now the number N is obviously equal to the number of collisions between iodine atoms per sec. per c.c.

$$= \sqrt{2} . \pi . S^2 . u . n^2$$

where S as before is the diameter of the neutral iodine atom and u, the *r. m. s.* velocity at the reaction temperature. Thus

$$\frac{2I_{abs}}{h\nu} = N = \sqrt{2} . \pi . S^2 . u . n^2$$

and $$n = \sqrt{\frac{2I_{abs}}{h\nu . \sqrt{2} . \pi . S^2 u}}.$$

Therefore $Z_1 = a^2 \sqrt{\left\{ 8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}} . n_s \sqrt{\frac{2I_{abs}}{h\nu . \sqrt{2} . \pi . S^2 . u}}$.

Substituting in this expression for the various quantities from Schumacher's data,

$a = 4{\cdot}0 \times 10^{-8}$ cm. ; $T = 100° = 373°$ Abs. ; $M_1 = 127$; $M_2 = 280$;

$$n_c = \frac{0{\cdot}088 \times 6{\cdot}06 \times 10^{23}}{1000}\ ; \quad I_{ab} = \frac{1{\cdot}97 \times 10^{15}}{55}\ \text{Quanta per c.c.};$$

$$n = 2{\cdot}70 \times 10^{4}\ \text{cm. per sec.}; \quad S = 2{\cdot}72 \times 10^{-8}\ \text{cm.}$$

Z_1 becomes equal to $1{\cdot}04 \times 10^{22}$ per c.c. per sec. and $Z_2 = 9{\cdot}0 \times 10^{14}$ per c.c. per sec. Then,

$$\frac{Z_2}{Z_1} = e^{-E/RT} = \frac{9{\cdot}0 \times 10^{14}}{1{\cdot}04 \times 10^{22}} = 8{\cdot}65 \times 10^{-8}$$

or $E = 12{\cdot}0$ Cals.

This value of 12·0 Cals. for E is in excellent agreement with that of 11·8 Cals. given by Schumacher and Wigg. We are aware of the fact that our estimate of the diameter of ethylene iodide molecule is subject to a large error. A simple calculation shows, however, that within wide limits ($a = 1 \times 10^{-8}$ to $1{\cdot}0 \times 10^{-7}$ cm.), the value of E varies only from 11·5 to 12·2 Cals.

SUMMARY.

Schumacher and Wiig's postulate that only one in five of the binary collisions between iodine atoms results in molecule formation, has been shown to be incorrect from their data on this reaction. On the other hand the evidence is very much in favour of the hypothesis put forward by us that every such collision does lead to molecule formation. The energy of reaction has been calculated on this basis and shown to agree very well with that observed.

My best thanks are due to Prof. J. C. Ghosh for his interest and suggestions.

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On the Measurement of the Absolute Rates of Migration of Ions by the Method of Moving Boundaries. Part I.

By Jnanendranath Mukherjee, Ramprasad Mitra and Anil Kumar Bhattacharyya.

The method of moving boundaries has been extensively adopted for determination of transference numbers of electrolytic ions (*cf.* MacInnes and Longsworth, *Chem. Reviews*, 1932, **11**, 171).* The absolute rate of migration of an ion can be obtained by the boundary method if the potential gradient under which it moves can be accurately measured. This principle is utilised in the measurement of the cataphoretic speeds of colloidal particles by the boundary method. Mukherjee (*Proc. Roy. Soc.*, 1923, **A, 103**, 102; *J. Indian Chem. Soc.*, 1925, **2**, 296; *J. Phys. Chem.*, 1932, **36**, 595; *Kolloid Z.*, 1932, **58**, 155) has discussed the errors in the procedures previously adopted and has devised a method, based on considerations of disturbing effects arising out of migration of ions at the boundary, which makes it possible to determine the cataphoretic speeds under known potential gradients at and near the boundary. The present paper deals with an application of the method to determination of absolute rates of migration of electrolytic ions. The method allows also to ascertain the changes taking place near the boundary and to compare the results with standard mobility data.

Theory underlying the Method.

Let us consider a boundary between a solution of hydrochloric acid and an equiconducting solution of picric acid (*vide* Fig. 1.). When a potential gradient acts across the boundary in the direction indicated, an adjustment of the concentration of the picric acid takes place such that a more dilute solution of concentration c', governed by the relation $c/T = c'/T'$, rises. c and c' denote the concentrations and T and T' the transference numbers respectively of the chloride and picrate ions. The concentration c remains unaltered.

* This paper gives a complete bibliography on the subject.

Under steady conditions let A and B be two fixed planes at right angles to the current, respectively in the upper hydrochloric and the lower picric acid solutions. Since the adjusted concentration of the picric acid layer is determined by the concentration of hydrochloric acid layer, the potential difference between the two planes, is given by

$$V = i \left[\sigma_1 (X - x) + \sigma_2 . x \right] \quad \ldots \quad \ldots \quad (1)$$

where i, is the constant current density employed ; σ_1 and σ_2 are respectively the specific resistances of layers of hydrochloric and picric acid solutions ; x is the distance between the boundary and the fixed plane in picric acid and X, the total distance between the planes.

From equation (1)

$$\left(\frac{\delta v}{\delta x} \right) = i (\sigma_2 - \sigma_1) = P \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

and $$\frac{\delta v}{\delta t} = i (\sigma_2 - \sigma_1) \frac{\delta x}{\delta t}$$

$$= i (\sigma_2 - \sigma_1) \times \text{the velocity of the boundary}$$

$$= Q \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

P and Q are constants independent respectively of the position of the boundary and time.

Also, the potential gradient in the picric acid layers, is given as,

$$i . \sigma_2 = i . \sigma_1 + \frac{\delta v}{\delta x} \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

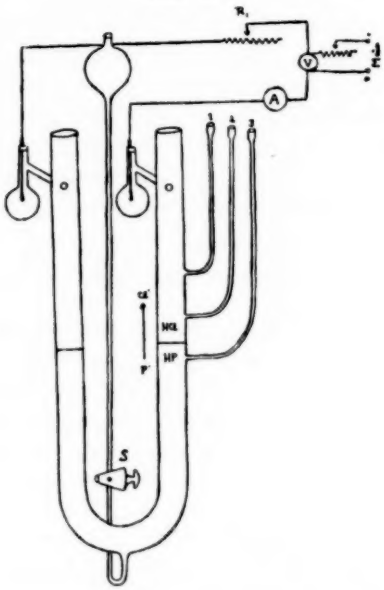
It is possible to measure the potential gradients in both layers without measuring the cross section of the tube if the potential gradient $i \sigma_1$ in the hydrochloric acid layer and $\delta v / \delta x$ are directly measured.

It follows from the above equations that if there are no disturbing effects, *e.g.* those arising from heating and diffusion, then

(*i*) the potential difference between the two planes should change linearly with time and also with the distance traversed by the boundary;

(*ii*) the distance swept should be linearly related with time.

FIG. 1.



EXPERIMENTAL.

Mukherjee's apparatus (Fig. 1) for measuring cataphoretic speeds of colloidal particles has been used. Rising boundaries between hydrochloric acid of different concentrations and picric acid solutions of correspondingly adjusted concentrations were investigated. The mobility of the picrate ion, as given in the literature, varies rather widely and is about half of that of the chlorine ion. The initial picric acid concentrations that have been used are exactly half of that of the hydrochloric acid solution. Picric acid exhibits a strong colour even in high dilutions and the boundary could be accurately located with the help of a selected light filter. The current from the main was tapped through a voltmeter and maintained constant within 1% by hand regulation of specially constructed adjustable resistances, R_1. An accurate ammeter directly reading upto 0·0001 amperes, placed in series with the measuring tube, indicated directly within 1 % of the current employed. The electrodes, through which the current entered and left the moving boundary cell, were placed in bulbs attached to either limb of the

U-tube. This prevented products of electrolysis from coming in contact with the solution in the U-tube. The boundary was formed as with colloidal solutions. In view of irregularities of cross section near the regions where the side-tubes are sealed, the boundary was always formed well above the side-limb 3 and the observation discontinued when it came sufficiently near the side-tube 2. Fairly wide tubes were used so that the electro-osmotic pressure developed on the passage of the current could be neglected.

Method of Calculation.

When the boundary is located between the side-limbs 2 and 3 (*cf.* Fig. 1) the difference in potential between two Ag—AgCl electrodes dipped into the side limbs 1 and 2 is measured. This potential difference remains constant within 0·2%. Knowing the effective distance between these side-limbs, the potential gradient in the upper hydrochloric acid is measured in the manner described previously (Mukherjee, *loc. cit.*). As the boundary rises the P. D. between 2 and 3 increases chronologically. The increment corresponding to a given displacement of the boundary is measured, from which the increment per centimetre displacement can be calculated; on adding this increment to the constant potential gradient obtaining in the upper HCl layer, the gradient in picric acid is obtained. By combining these gradients with the distance traversed by the boundary in a given interval of time, the absolute rates of migration of the chloride and also the picrate ions are obtained. The effective distance between the side-tubes was measured in the manner described previously. The values obtained agree within 1·73% : 2·90 and 2·95 cm. between 1 and 2. The two values were obtained by using 0·01*N* and 0·002*N*-HCl solutions. The difference is partly due to the fact that when the resistance of the electrolyte is high, apart from troubles due to dielectric leakage, the electrolyte in the immediate neighbourhood of the electrodes does not uniformly take part in the conduction (Mukherjee, *J. Phys. Chem.*, 1932, **36**, 595).

Satisfactory Boundary Conditions.

For a satisfactory measurement by this method the boundary must be *sharp and horizontal to start with*. The ideal condition of a perfectly sharp boundary is not always easy to attain in view of dis-

turbances due to heating and diffusion at the boundary. The initial condition of the boundary is an important factor. Thus if the two liquids get mixed owing to filling the tube too rapidly, the restoring effect on passing the current is often not sufficiently strong to make the boundary adequately sharp. The strength of the current to be employed for this purpose is necessarily limited by the heating effects. In these measurements dilute solutions (particularly in the case of 0·002*N*-HCl and 0·001*N*- picric acid) present the greatest difficulties in keeping the boundary horizontal. It has a tendency to become convex upwards. In extreme cases the passage of the current is accompanied by a chimney-shaped column of picric acid emerging from the boundary and penetrating deep into the upper liquid; similar phenomena have been observed by MacInnes, Cowperthwaite and Huang (*J. Amer. Chem. Soc.*, 1927, **49**, 1710) with rising boundaries between KCl and $KMnO_4$ solutions. Disturbances owing to the above effect were much less prominent when the current was gradually increased to its final value.

The $V-x$, $V-t$, and $x-t$ Curves.

The accompanying curves I—X show that the value for $\delta v/\delta x$, $\delta x/\delta t$ and $\delta v/\delta t$ are not exactly constant as required by the equations (2) and (3). The discrepancy must be referred to the disturbing influences at the boundary owing to which the conditions implied in the linear equations are not satisfied.

Results.—The results of experiments which satisfied the criteria for satisfactory boundary conditions are given in Table I. The first column gives the combination; the second, the potential gradient in volt/cm. in the hydrochloric acid layer between side-limbs 1 and 2, the boundary was always initially formed between side-limbs 2 and 3; the third column gives the potential gradient in layers of picric acid calculated from equation (4), $\delta v/\delta x$ being obtained from the slope of the corresponding curve; the fourth column gives the mobilities (in cm./sec. per volt/cm.) of the Cl' ion calculated from the constant potential gradient in the hydrochloric acid layer and the distances traversed by the boundary in successive known intervals of time; the fifth column gives the chloride ion mobility in cm./sec. per volt/cm. calculated from the measured potential gradient in HCl and the average velocity of the boundary given by the corresponding $x-t$ curve. The sixth column gives the values of the picrate ion mobility (in cm./sec. per volt/cm.) calculated from measurements of distances

traversed by the boundary in successive known intervals of time and the corresponding potential gradients in picric acid layers. The last column gives the picrate ion mobility (in cm./sec. per volt/cm.) calculated by combining the graphically calculated average potential gradient in picric acid layers behind the boundary and the average velocity of the boundary given by the slope of the corresponding $x-t$ curve.

TABLE I.

Temperature $= 35 \pm 0.025°$.

Combination.	Pot. gradient. in HCl.	Pot. gradient. in HP (from graph).	$v_{cl'} \times 10^5$ (calc.)	$v_{cl'} \times 10^5$ (from graph).	$v_{p'} \times 10^5$ (calc.)	$v_{p'} \times 10^5$ (from graph).
I*. 0·01*N*-HCl, 0·005*N*-HP	0·8658	1·73	79·4 78·6	78·5	38·01 39·36	39·3
II. 0·01*N*-HCl, 0·005*N*-HP	0·8688	1·81	80·8 80·2	80·6	38·18 38·7	38·7
III. 0·01*N*-HCl, 0·005*N*-HP	0·8545	1·77	80·2	80·0	38·65	38·4
IV. 0·005*N*-HCl, 0·0025*N*-HP	1·330	2·67	84·3 84·1	84·2	41·5 42·5	41·9
V. 0·005*N*-HCl, 0·0025*N*-HP	1·332	2·69	84·0 84·3	84·3	42·3 44·8	42·7
VI. 0·005*N*-HCl, 0·0025*N*-HP	1·224	2·35	83·3 81·9 81·2	82·5	42·5 42·4 45·4	42·1
VII. 0·005*N*-HCl, 0·0025*N*-HP	1·223	2·26	82·5 82·2	82·6	41·9 51·0	44·7
VIII. 0·005*N*-HCl, 0·0025*N* HP	0·8081	1·69	81·9 80·7	80·5	40·01 36·70	38·6
IX. 0·002*N*-HCl, 0·001*N*-HP	1·003	2·08	86·8 81·2	86·0	41·1 49·1	41·5
X. 0·002*N*-HCl, 0·001*N*-HP	1·058	2·13	89·4 82·6	88·2	43·3 45·3	43·6

DISCUSSION.

The method here adopted should give a more direct information of the boundary conditions than the usual method. Also, it enables one to calculate the rates of migration of both the leading and the indicator ions.

* The curves are correspondingly numbered.

FIG. 2.

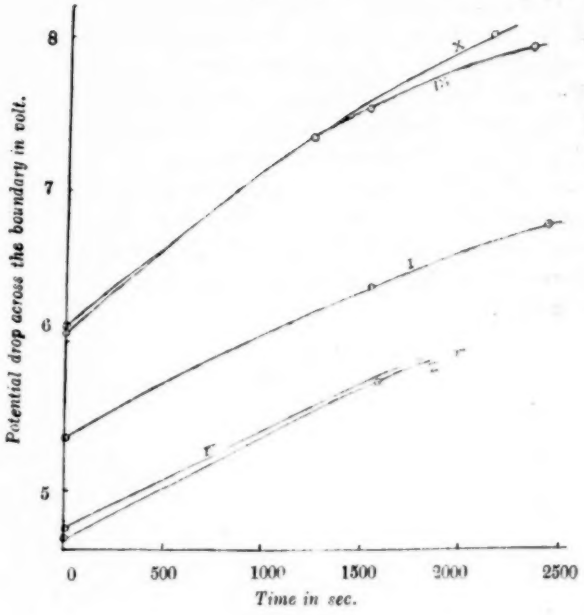
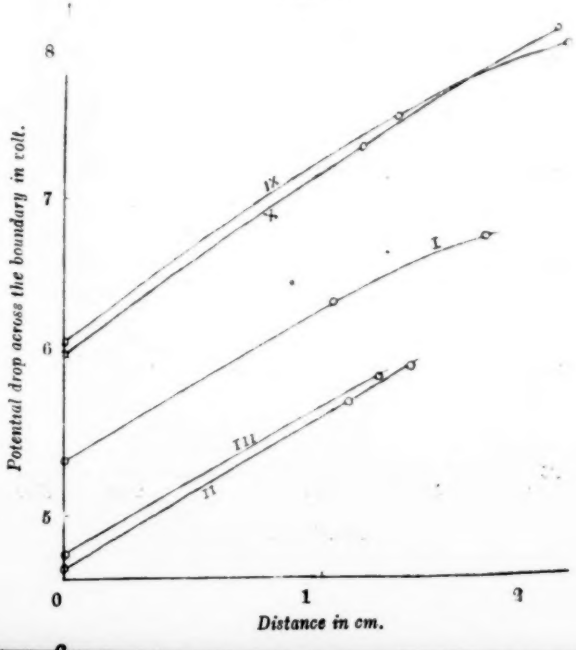
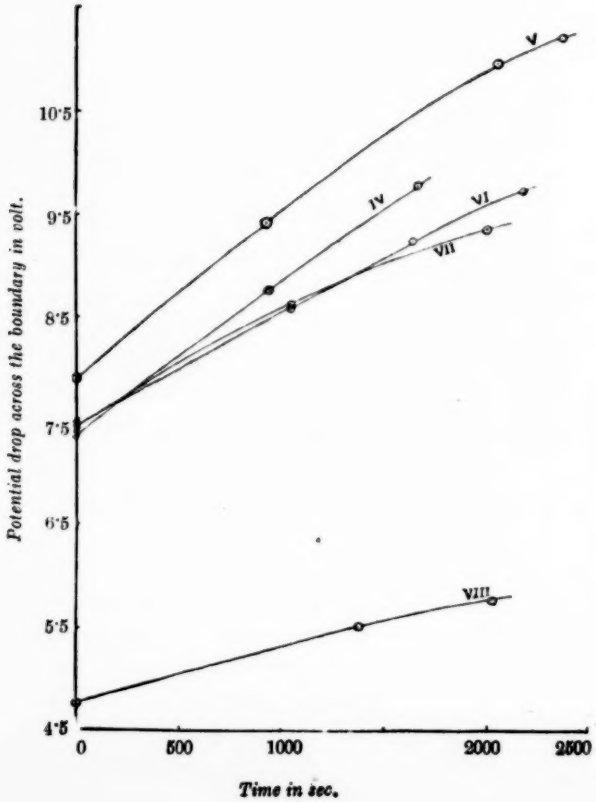

8
7
6
5
Potential drop across the boundary in volt.
0
500
1000
1500
2000
2500
Time in sec.

FIG. 3


8
7
6
5
Potential drop across the boundary in volt.
0
1
2
Distance in cm.

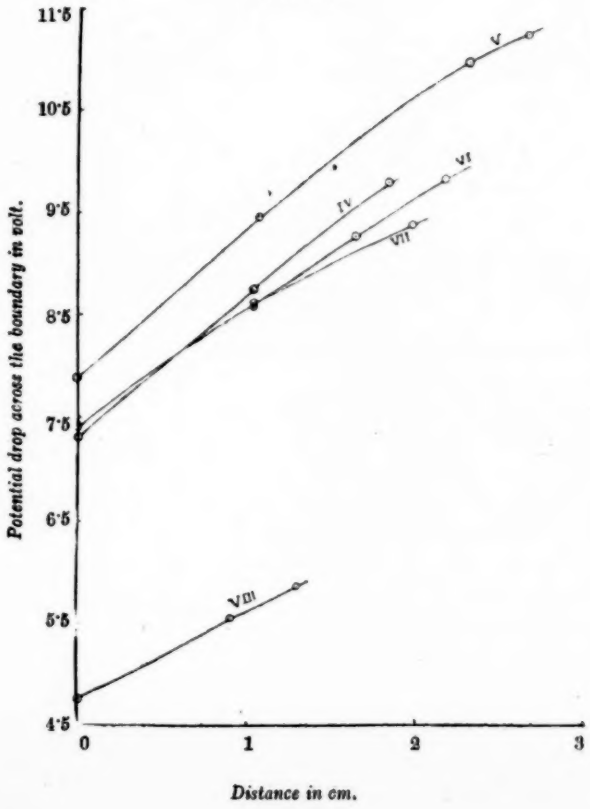
The results show that in a particular measurement the mobility of the chloride ion calculated from chronological observations of the displacement of the boundary tends to decrease while the picrate ion mobility tends to increase. At the same time the slopes of the corresponding $V-x$ and $x-t$ curves show a general tendency to decrease; $\delta v/\delta x$ and $\delta x/\delta t$ tend to decrease with time. The decrease in chloride ion mobility and the simultaneous increase in the mobilty of the picrate ion would at first sugg est that the hydrochloric acid is becoming concentrated and the picric acid diluted so that the boundary separates two pure layers of hydrochloric and picric acids ; the chlorine and the picrate ions in these layers move under potential gradients obtaining in them.

FIG. 4.



Kohlrausch's theory, however, contemplates no changes in the concentration of the leading solution. Besides, such changes cannot account for the diminution of $\delta v/\delta x$ observed by us. In the neighbourhood of adjusted concentrations, if the current remains constant and disturbances arising from thermal and gravitational convection are absent, a sharp boundary has been observed to move (MacInnes and Longsworth, *Chem. Reviews*, 1932, **11**, 171) with a constant velocity for fairly long intervals of time. In the present case the boundary slows down though the decrease is much less pronounced than the decrease in $\delta v/\delta x$. If the electrolysis be continued for a sufficient length of time the boundary becomes diffuse and hazy.

FIG. 5.



The decrease of $\delta v/\delta x$ for a constant current density connotes the following possibilities (*vide* equation 2).

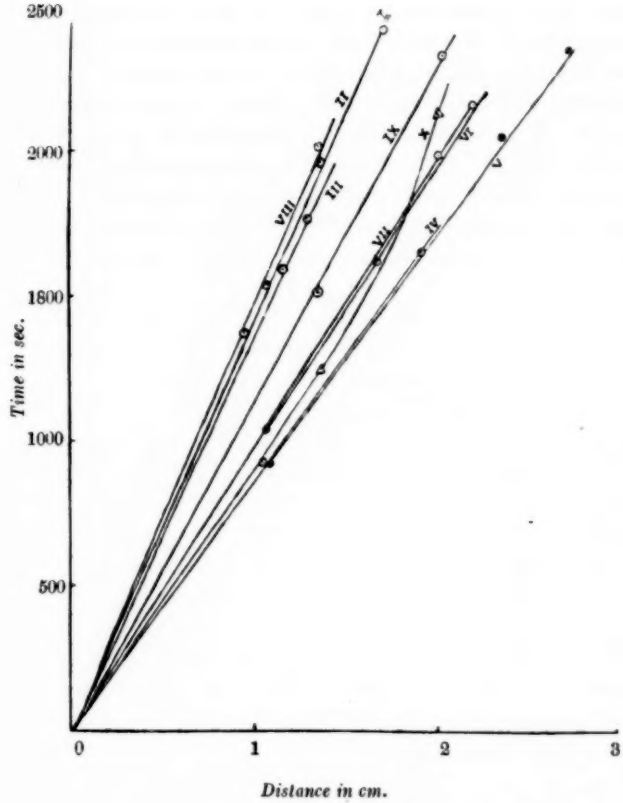
1. σHCl increases, σHP remaining constant,
2. σHP decreases, σHCl remaining constant,
3. σHP decreases, and σ HCl increases.

Since the potential gradient between side-limbs 1 and 2 remains constant and the values of the calculated mobility of the Cl' ion decrease, the first possibility is excluded. The gradual increase of the calculated mobilities of the picrate ions also excludes the second possibility and consequently the third. The cause of the variation of $\delta v/\delta x$ should, therefore, be sought in the boundary itself. A mixed layer whose thickness gradually increases is perhaps responsible for the progressive diminution in $\delta v/\delta x$. But since the velocity of the boundary itself gradually slows down, it is necessary to assume that the potential gradient at the boundary diminishes; that is, the layer becomes more conducting and more concentrated in electrolytes. This would also explain the diminution in the calculated mobilities of the Cl' ion. It should be mentioned however, that *the boundary remains sharp during the period of observation which has been utilised in calculating the data given in the table.* This may not prevent slight mixture brought about by thermal convection or by diffusion. The mobility of the chlorine ions calculated as above would in that case be determined by their speed in this mixed layer. The values would thus be smaller than the actual mobility because a higher potential gradient, namely that in the pure HCl layer has been used in the calculation.

Reference should be made here to the fact that the introduction of the current at first makes the boundary sharp but as the electrolysis proceeds sufficiently long, the boundary becomes hazy. It may, therefore, be assumed that the restoring effect is initially sufficient but that the heating effect of the current produces thermal convection and increased diffusion which nullifies the restoring effect. It is thus possible that even during the earlier period, during which the recorded observations were made, a mixed layer of the two electrolytes was present.

The existence of such a mixed layer whose thickness and concentration gradually increase would explain the chronological increase in the values of the picrate ion mobility. For, the potential gradient

FIG. 6.



obtained from equation (4) used in the calculation would then be progressively smaller ($\delta v/\delta x$ gradually decreases) than the gradient under which the anion moves. We are assuming that the boundary, whose displacement we observe, is situated just inside the mixed layer. The presence of such a mixed layer of higher total ionic concentration than that of the hydrochloric or picric acid layers may, however, lead to other complications which are being ignored for the present.

The above considerations show that the mobilities calculated from the initial slopes $\delta v/\delta x$ and $\delta x/\delta t$ are the most reliable and a comparison should be made only amongst them. The third column of Table II gives the observed (mean) chlorine ion mobility ($F \times vcl'$) in

hydrochloric acid whose strength in normality is given in column 1. The fourth column gives the theoretical value at the corresponding HCl concentration calculated from Onsager's equation* assuming 92·6** as the limiting Cl′ ion mobility at 35° ; the fifth column gives the percentage deviation of the observed mean value from the calculated value ; the sixth column gives the observed mean picrate ion mobility (in cm./sec. per volt/cm.) in the corresponding picric acid solution. In view of different limiting picrate ion mobilities and also of different temperature coefficients given in the literature, similar comparison of observed with calculated values is not possible.

TABLE II.

HCl conc.	$v_{cl'} \times 10^5$. (obs.)	$v_{cl'}$ mean $F \times v_{cl'}$(mean)	$v_{cl'}$ calc.	% Diff.	$v_{p'} \times 10^5$. (Obs. mean).
0·01*N*	79·4 80·8 80·2	77·4	87·0	12·4	38·3
0·005*N*	84·3 84·0 83·3 82·5 81·9	80·4	88·8	10·4	41·6
0·002*N*	86·8 89·4	85·1	90·3	6·1	42·2

The observed Cl′ ion mobilities are distinctly lower. The discrepancy appears to be greater for concentrated than for dilute solutions though initial satisfactory boundary conditions were more easy to attain in the former cases. Higher current densities had to be employed to obtain sharp boundaries with the concentrated solutions; the higher concentrations would produce more rapid diffusion.

* $\lambda = \lambda_0 - \left[\frac{5{\cdot}78 \times 10^5}{(DT)^{\frac{3}{2}}} \lambda_0 + \frac{29{\cdot}5}{(DT)^{\frac{1}{2}}\eta} \right] \sqrt{2C}$, where λ_0, D, T, η and C are respectively the limiting mobility, the dielectric constant of the solvent, the absolute temperature, the viscosity of the solvent and the equivalent concentration.

** $V_{cl'}^{\infty}$ at 25° (Ferguson and Vogel, *Phil. Mag.*, 1927, **4**, 940) = 76·63 ; assuming a temperature coefficient of 2·16% (Newman, "Electrolytic Conduction", 1930, p. 49) it is 92·6 at 35°.

The mobilities appear to depend on the potential gradient in the hydrochloric acid layer though Kohlrausch's theory contemplates no effect of the current provided that the restoring effect is strong enough to give a sharp boundary. MacInnes and Smith (*J. Amer. Chem. Soc.*, 1923, **45**, 2246) and Cady and Longsworth (*ibid.*, 1929, **51**, 1656) made similar observations but no explanation of this effect of the current has been given. The calculated mobility is less, the less the potential gradient in hydrochloric acid. Since the heating effect is comparatively small the lower value perhaps indicates that the restoring effect of the weaker current is insufficient to prevent diffusion. The current density is thus a very important factor.

The above discussion suggests that the moving boundary method should give better results when the displacement of the boundary is utilised in the calculation. The speed of the boundary $\delta x/\delta t$ changes much less than $\delta v/\delta x$ and methods which depend on the boundary speed alone, would be free from the errors arising out of the uncertainties regarding the potential gradient obtaining at the boundary. In measuring the cataphoretic speeds of colloidal particles by the method here adopted, the above errors are practically eliminated by choosing the upper liquid such that the potential gradient across the boundary remains constant during both the upward and downward movements (Mukherjee, *loc. cit.*, also *J. Phys. Chem.*, 1932, **36**, 595).

It appears that diffusion and thermal convection affect the thickness of the boundary as also its rate of motion and that for a constant current the mixed layer does not move with the same speed as the 'fully formed boundary.'' These observations are not in agreement with those of MacInnes and Longsworth (*loc. cit.*).

It is hoped to revert to the points referred to above when experiments now in progress are completed.

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Magnetic Susceptibilities of Cobaltic Salts and the Nature of the Cobaltic Ion.

By Priyadaranjan Rây and Dines Chandra Sen.

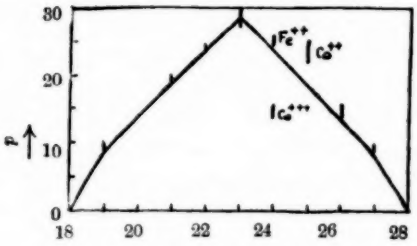
Though it has long been established that all complex cobaltic compounds are diamagnetic, the susceptibility value for the simple Co^{+++} is, however, not definitely known, due evidently to the difficulty of preparing simple cobaltic salts in the pure and solid state. The only measurement, recorded in literature, refers to a solution of cobaltic sulphate prepared by anodic oxidation of cobaltous sulphate solution (Weber, *Ann. Physik*, 1911, **36**, 624), which, as the author himself admits, was far from pure. The value obtained was about 16·73 Weiss's magneton. Wilson, also, obtained a value of 12·9 Weiss's magneton for Co_2O_3 (*Proc. Roy. Soc.*, 1921, **A**, **98**, 274). But as Co_2O_3 can seldom be obtained in a pure state, free from other oxides of cobalt, apart from the fact that black sulphides and oxides of metals often assume metallic character and show a much lower susceptibility value than that of the free corresponding ions (Klemm and Schüth, *Z. anorg. Chem.*, 1931, **203**, 104 ; 1933, **210**, 43), it was considered of special interest to determine, if possible, a more or less exact value for this ion. We have prepared a number of apparently simple cobaltic salts in the solid state and have measured their susceptibility values. They all approximate to 2 Bohr's magneton number, a value which Weber's measurement in solution tends to approach. The salts examined are anhydrous and hydrated cobaltic cyanide, cobaltic sulphate and cobaltic alum.

It is well known that the susceptibility value for the Co^{++} is given by 23·25 Weiss's magneton, or approximately 4 Bohr's magneton. The ionic susceptibilities of the elements of the first transitional series are given more or less satisfactorily by the expression,

$$p = 4{\cdot}97\sqrt{4S(S+1)}$$

according to Bose and Stoner (Bose, *Z. Physik*, 1927, **43**, 864; Stoner, *Phil. Mag.*, 1929, **8**, 250), where p = Weiss's magneton

number and S = resultant spin moment, the resultant orbital moment, L, is rendered ineffective due to strong interaction with the neighbouring ions. The actual experimental values and those calculated on the basis of the above formula are shown in the following figure.



No. of extranuclear electrons.

[Calculated moments are given by the curve. The thick vertical lines indicate the range of observed values.]

The first half of the series shows quite good agreement, the last half, on the other hand, reveals an appreciable deviation (actual values being higher), and the moments of the ions in this half extend over a short range suggesting that the L-interaction may take place to different extents in different compounds and is not strong enough to render the L-moment completely inoperative.

On this view, the Co^{+++} with an extranuclear electron number of 24 should possess a magnetic moment of 24·4 Weiss's magneton (4 Bohr's magneton), or a little higher than this, due to imperfect L-interaction. The actual value, obtained in the case of above cobaltic compounds, is, however, equal to 2 Bohr's magneton approximately. This is quite anomalous and demands a satisfactory explanation.

In the first place, it may be suggested that the compounds do not possess a simple constitution. Thus, for instance, $Co(CN)_3$ and its hydrate may be regarded as a complex cobaltic cobalticyanide $Co^{m}[Co^{m}(CN)_6]$. The complex anion, as is well known, being diamagnetic, the magnetic moment of the molecule will be contributed by only one of the Co-atoms in the free ionic state as Co^{+++}. Hence the atomic or ionic moment should come out as half the theoretical value.

On the other hand, there is little evidence or justification to assume that cobaltic sulphate and cobaltic alum, also, are made up of complex anions of the perfect order, represented as $Co^{III}[Co^{III}(SO_4)_3]$. But, as the cobaltic alum is isomorphous with other alums, it must possess a similar composition and constitution. Further, the normal chemical behaviour of these two substances militate against the assumption of any complexity of high order in their molecule. They should consequently be regarded as simple and double salt respectively, and their magnetic moment represents the true value for the simple Co^{+++} ion. But this, again, raises a question of great theoretical interest, as the observed moment is about half the expected theoretical value, even allowing for the perfect or complete *L*-interaction.

The Co^{+++} ion, however, is extremely unstable, readily changing into Co^{++} by the capture of an electron. Hence the electronic structure of the unstable Co^{+++} cannot represent its deepest state. The fundamental spectral terms for the two ions, Co^{++} and Co^{+++}, should be ^4F and ^5D respectively, the corresponding electronic groups being d^7 and d^6. This should give a moment of at least 4 Bohr's magneton for the Co^{+++} identical with that for Fe^{++}, which is, however, not the case. This seems to suggest that the Co^{+++} in the above mentioned cobaltic salts is in an excited or metastable state, which should be represented by a spectral term other than ^5D. In other words, the electronic state of the Co^{++} seems to persist in the Co^{+++}, even after the removal of an additional unbalanced electron by oxidation, no redistribution of electrons, leading to the lowest energy state, occurring during the transformation of Co^{++} into Co^{+++} ion. This would give a triplet term for Co^{+++}. Hence $S=1$, and $p=4{\cdot}97\sqrt{4\times1\times2}=14{\cdot}01$. This is in very good agreement with the experimental values.

It may, therefore, be concluded that in these cobaltic salts the cobaltic ion is in a metastable or higher energy state, which accounts for its instability and anomalous magnetic moment.

Experimental.

Cobaltic cyanides.—Both the red hydrated and the blue anhydrous compounds were prepared according to the method described by Rây and Gupta-Chaudhury (*Z. anorg. Chem.*, 1934, **220**, 162).

Blue anhydrous. [Found: Co, 42·9; CN, 57·2. $Co(CN)_3$ requires Co, 43·1; CN, 56·9 per cent]. $\chi_m\ (t_{31})=22{\cdot}31\times10^{-6}$; $p_{Weiss}=13{\cdot}58$; p_{Weiss} corrected $=13{\cdot}63$.

Red hydrated. [Found: Co, 34·22; H_2O, 20·60. Co $(CN)_3$, $2H_2O$ requires Co, 34·10; H_2O, 20·81 per cent]. $\chi_m\ (t_{30}) = 21{\cdot}79 \times 10^{-6}$; $p_{Weiss} = 15{\cdot}04$; p_{Weiss} corrected $= 15{\cdot}16$.

Cobaltic alum was prepared according to the method described by Marshall (*J. Chem. Soc.*, 1891 **59**, 760) by electrolysis in a divided cell in the cold. The large blue crystals were removed, rapidly dried by means of filter paper and examined at once in a Curie's balance. [Found: Co, 11·98. $Co_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ requires Co, 12·16 per cent]. $\chi_m\ (t_{31}) = 6{\cdot}48 \times 10^{-6}$; $p_{Weiss} = 13{\cdot}76$; p_{Weiss} corrected $= 14{\cdot}29$.

Cobaltic sulphate was prepared by electrolysis in the cold in a divided cell as described by Copeaux (*Compt. rend.*, 1905 **140**, 657). The blue crystals were dried and examined as before. $\chi_m\ (t_{30}) = 11{\cdot}28 \times 10^{-6}$; $p_{Weiss} = 15{\cdot}71$; p_{Weiss} corrected $= 16{\cdot}05$.

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The Complex Formation between Manganese or Aluminium with Tartaric Acid in Alkaline Medium.

BY S. P. GOVEL AND B. L. VAISHYA.

The present work is in continuation of the work carried out by Raman and Vaishya on complex formation between cerium or tungsten with tartaric acid in alkaline media (*J. Indian Chem. Soc.*, 1934, **11**, 179).

EXPERIMENTAL.

In order to work with manganese chloride and potassium tartrate in alkaline solution and to ensure that no precipitate is formed under ordinary circumstances, it is found to be essential to add only sufficient quantity of alkali so that the whole of the manganese salt is transformed into hydroxide and there is only slight

excess of alkali. The solution thus prepared was found to have a colour which deepens on keeping. The solution, it was found, could be rendered colourless by exposure to the sun and would continue to be colourless if kept out of contact of air and not otherwise.

Table I gives the results obtained with the polarimeter. The optical rotation goes on decreasing and reaches a minimum when the solution contains 1 mol of potassium tartrate to 1 mol of manganese oxide. The effect of temperature is clear from Table II. Table III contains the results obtained by the *e.m.f.* method. The p_H was found to show a rapid change at the same place at which complex formation is observed.

Manganese Oxide and Potassium Tartrate.

TABLE I.

K-tartrate = 3·39 g./100 c.c.

MnO.	K-tart. : MnO.	$a_D^{15.}$	$[a]_D^{15.}$
0·0000 g./100 c.c.	1 : 0·0	1·9°	28·62°
0·2173	1 : 0·166	1·4	19·40
0·4346	1 : 0·333	1·2	15·70
0·6519	1 : 0·500	1·1	13·60
0·8692	1 : 0·666	1·0	11·70
1·0865	1 : 0·833	0·9	10·04
1·3038	1 : 1·000	0·7	7·40
1·5211	1 : 1·166	0·7	7·10

TABLE II.

Temp.	...	15°	25°	34°
a_D	...	0·7°	1·0°	1·2°
$[a]_D$	...	7·4°	10·6°	12·7°

TABLE III.

Molar prop. of K-tart : MnO	...	1 :0	1 :·166	1 :·333	1:·5	1 :·666	1 :·833	1 :1	1 :1·166
p_H	...	13·14	12·93	12·90	12·85	12·77	12·51	12·07	12·29

TABLE IV.

Aluminium sulphate and potassium tartrate.

K-tartrate = 1 695 g./100 c.c.

Al_2O_3.	K-tart. : Al_2O_3.	α_D^{15}.	$[\alpha]_D^{15}$.
0·0000 g./100 c.c.	1 : 0·000	0·9°	26·54°
0·1274	1 : 0·166	1·0	27·47
0·2548	1 : 0·333	1·2	30·76
0·3821	1 : 0·500	1·4	33·65
0·5095	1 : 0·666	1·5	34·09
0·6369	1 : 0·833	1·5	32·19
0·7642	1 : 1·000	1·5	30·48

TABLE V.

Aluminium sulphate and sodium tartrate.

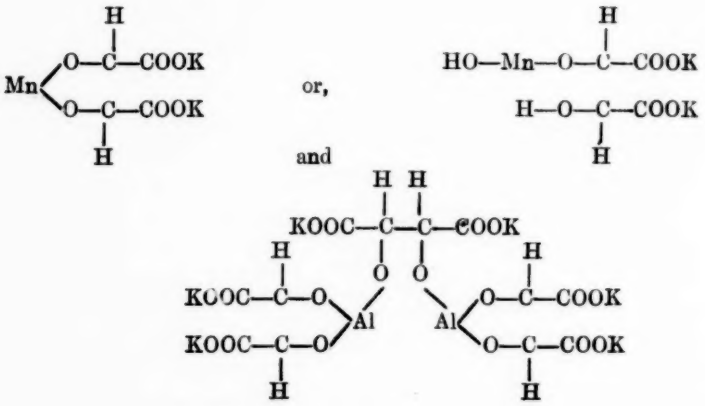
Na-tartrate = 2·91 g./100 c.c.

Al_2O_3.	Na-tart. : Al_2O_3.	α_D^{15}.	$[\alpha]_D^{15}$.
0·0000 g./100 c.c.	1 : 0·000	1·8°	30·92°
0·2548	1 : 0·166	1·9	30·06
0·5095	1 : 0·333	2·0	29·24
0·7643	1 : 0·500	2·1	28·60
1·0190	1 : 0·666	2·3	29·26
1·2738	1 : 0·833	2·3	27·50
1·5285	1 : 1·000	2·3	25·20

Table V gives the results obtained with the polarimeter. It has been observed that *p* value results and the polarimeter investigations indicate the formation of complexes.

Conclusion.

Oxides of manganese and aluminium form complex with potassium tartrate in the ratio of 1:1 and 2:3 respectively. According to the view held by Dermois (*Bull. Soc. chim. Belg.*, 1927, **36**, 64) the compounds will be of the type,



Summary.

1. The complex formation between potassium tartrate and manganese chloride was studied in alkaline medium by means of polarimeter and potentiometer and it was found that a complex formation thus takes place when the molar proportions of potassium tartrate and manganese chloride is 1:1.

2. The formation of complex between alkali tartrate and aluminium sulphate in alkaline medium was also studied. The complex formation in this case is with two molecules of aluminium sulphate and three molecules of tartrate as found out by Yeu-ki-Heng (*Compt. rend.*, 1933, **196**,259).

Our thanks are due to Mr. Jang Bahadur Jha who very kindly helped us in determining the p_H values.

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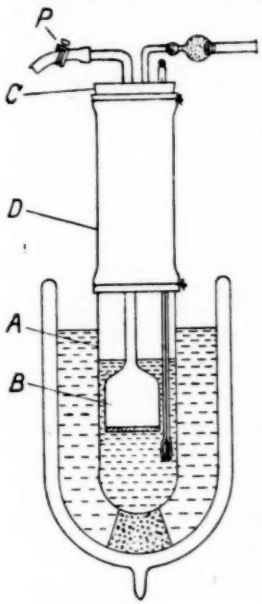
A Simple Apparatus for Fractional Solidification.

By R. Padmanabhan.

In fractionally freezing out a mixture so as to separate it into its components it is found that the efficiency of the separation depends largely on vigorous stirring when solidification takes place. When the experiment is carried out at low temperatures, it is better for the substance to be out of contact with air so that contamination with atmospheric moisture may be prevented. The method described below is found to work satisfactorily in practice and the separation of the solid from the portion still liquid is more efficiently being done *in situ*, while there is no chance for entry of atmospheric moisture.

A is a wide test tube and B an immersion filter which serves also as a stirrer. The cork C is attached to the test tube by a short piece of cycle tubing D, which allows the filter to be moved up and down. The cork also carries a calcium chloride tube and a thermometer. In order to prevent the substance getting into the filter, it is kept filled with some inert gas under slight pressure by its end being connected to a carbon dioxide Kipp. When the material is partial y frozen by the tube being immersed in a suitable freezing mixture, suction is applied to the end of the immersion filter till all the unsolidified portion is taken up in the filter and carbon dioxide begins to bubble through. The filter is then slightly raised and the pinch-cock P screwed down. If now the test tube is allowed to warm up to room temperature, the contents can be poured out without any condensation of moisture on the substance taking place.



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Use of Vanadous Sulphate as a Reducing Agent. Part I.

By Pares Chandra Banerjee

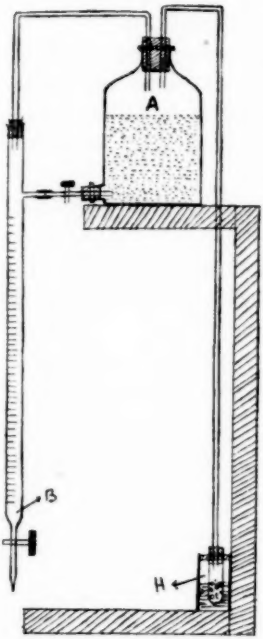
It seems that no systematic study has been made on the reducing property of vanadous salts. Though it has been stated by Piccini, and others (Piccini, *Z. anorg. Chem.*, 1899, **19**, 204; Piccini and Marino, *ibid.*, 1902, **32**, 55; Marino, *ibid.*, 1906, **50**, 49; Rutter, *ibid.*, 1907, **52**, 368) that salts of copper, silver, tin, gold, platinum and mercury are reduced to the metal by the vanadous salts; but these investigations are more or less qualitative. Russel (*J. Chem. Soc.*, 1926, 497) has published a note stating that vanadous sulphate is a more powerful reducing agent than titanous sulphate, reducing with greater ease all the inorganic and organic substances reduced by the latter. Russel, however, did not give any experimental evidence in support of his statement. Konrad and Masse (*Z anal. Chem.*, 1934, **97**, 241) have recently published a paper on the use of divalent vanadium salt as a reducing agent in potentiometric analysis. The object of the present investigation is to make a quantitative study on the reducing action of vanadous sulphate upon various inorganic and organic substances and to see whether it can be used as an analytical reagent in volumetric analysis.

Experimental.

Preparation of vanadous sulphate.—Vanadous sulphate is very easily oxidised by air. Its double salt with ammonium sulphate is however more stable. Hence a solution of vanadous ammonium sulphate $VSO_4(NH_4)_2SO_4, 6H_2O$ was used as the reducing agent. It was prepared by the electrolytic reduction of vanadyl sulphate in presence of ammonium sulphate as follows (*cf.* Muller, "Elektrochemische Practikum," 1920).

Apparatus.—The electrolytic vessel consisted of a thick walled cylindrical battery glass jar of 9 cm. height and 7 cm. diameter. This was closed with a rubber cork through which passed a porous clay cylinder of 12 cm. high and 4·5 cm. in diameter. The anode consisted of a lead foil in the form of a cylinder and was placed into the porous cell. Surrounding the clay cylinder was the cathode consisting of a lead cylinder of 4 cm. high. *Catholyt* consisted of a solution of vanadyl sulphate in sulphuric acid containing some ammonium sulphate and *anolyt* consisted of 1 part of concentrated sulphuric acid mixed with 2 parts of water.

FIG. 1.



A—Aspirator. B—Burette.
H—Hydrogen generator.

The vanadyl salt was reduced by passing a current of 4 amp. from a series of storage cells having an *e.m.f.* of 30 volts. Carbon dioxide was all along passed during electrolysis. Reduction was complete in course of 2-3 hours when the colour of the solution gradually changed from blue to green and finally to violet or lavender. The solution from the electrolytic vessel was then transferred into a storage bottle which had been previously freed from air by passing a current of carbon dioxide. The solution was diluted with air-free cold water and sufficient sulphuric acid so that it was about 2*N* with respect to sulphuric acid and 0·1*N* with respect to ferric salt. The solution was preserved in an atmosphere of hydrogen. An arrangement of the apparatus for using the reagent is shown in Fig. 1.

Some Qualitative Reactions of Vanadous Sulphate.

The reducing action of vanadous salts is in the great majority of cases, far more energetic than that of other acid reducing agents. With strong nitric acid it reacts violently with evolution of nitrous fumes. Potassium nitrate in presence of hydrochloric acid is reduced

with the formation of nitric oxide. Chlorates are reduced to chlorides. Salts of persulphuric acid are reduced to sulphates. Sulphurous acid is instantaneously reduced to hydrosulphurous acid with the formation of sulphuretted hydrogen and free sulphur. Ferric salts are reduced to ferrous salts. Ceric salts are reduced to cerous state.

Among organic substances nitro compounds (*e.g.*, nitrobenzene, nitrotoluene, picric acid, etc.) are reduced to corresponding amino compounds. Aldehydes and ketones are reduced to corresponding alcohols (*cf.* Connaut and Cutter, *J. Amer. Chem. Soc.*, 1926, **48**, 1019).

Among organic dyes, indigo, methylene blue, safranine, congo red, malachite green, auramine primuline and practically all the dyestuffs which are capable of yielding *leuco* compounds are reduced by the reagent. In most of these cases, as will be shown later on, the reduction is quantitative.

Application of the Vanadous salt in Quantitative Analysis.

The solution was first of all standardised. For this purpose 25 c.c. of a standard solution (0·1*N*) of ferrous ammonium sulphate were carefully oxidised with potassium permanganate of about *N*/50 strength until a faint pink colouration was obtained A large excess of potassium sulphocyanide was then added and the ferric iron titrated with the vanadous sulphate in an atmosphere of carbon dioxide until the red colouration due to ferric sulphocyanide entirely disappeared. In order to avoid the necessity of oxidising ferrous ammonium sulphate with permanganate for every standardisation, a large volume (about 2 litres) of a standard iron alum solution was prepared The iron alum solution which retained the same strength for indefinite period was used in all subsequent cases for standardising the vanadous sulphate olution.

Estimation of Iron.

Solutions of ferric iron may be titrated directly with vanadous sulphate solution, using an excess of potassium sulphocyanide as inside indicator. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, because the sulphocyanide indicator is otherwise not sensitive. For the estimation of ferrous iron it must be first oxidised to the ferric state and then titrated.

Estimation of iron in iron wire.—Merck's G. R. steel wire (1·4g) was dissolved in sulphuric acid and the solution was made up to 250 c. c. A known volume of this solution was just oxidised with potassium permanganate and then titrated with the vanadous salt.

TABLE I.

Strength of vanadous soln. = 0·7776*N*/10. 1 C. c. = 0·004354 g. Fe.

	Vol. of iron soln.	Vol. of vanadous salt reqd.	Amount of iron in the wire.
1.	25 c. c.	32·05 c. c.	99·7 %
2.	25	32·0	99·5
3.	20	25·65	99·5
4.	30	38·50	99·8

Estimation of iron in hæmatite.—Finely powdered sample of the ore (2 g.) was dissolved in hydrochloric acid and the solution made up to 250 c. c. 25 C. c. of this solution were treated with ammonia and hydrogen peroxide, boiled, acidified strongly with sulphuric acid and then titrated with vanadous sulphate using sulphocyanide as an indicator.

TABLE II.

Strength of vanadous soln. = 1·48*N*/10. 1 C. c. = 0·008288 g. Fe.

	Vol. of iron soln.	Vol. of vanadous soln.	Amount of iron found.	Found by dichromate method.
1.	25 c. c.	15·2 c. c.	62·98%	
2.	25	15·15	62·80	62·90%
3.	25	15·15	62·80	

Estimation of Copper.

A known volume of a standard solution of copper sulphate was mixed with a known amount of the standard ferric alum solution and an excess of potassium sulphocyanide. The mixture was titrated with the vanadous sulphate when the copper was first precipitated as white

cuprous sulphocyanide and then the red ferric sulphocyanide was reduced to colourless ferrous salt which remained in solution. The amount of potassium sulphocyanide must be in excess, and as long as this was the case varying amounts of this reagent did not affect the results. By subtracting the volume of the vanadous salt required for the known amount of iron from the total volume, the amount of vanadous salt used for reduciug copper was found out.

Experiment, however, having shown that cupric salts are readily reduced by ferrous salts in acid solution and that the amount of vanadous sulphate used in a copper estimation was the same with or without the addition of pure ferrous salt, the mode of titration was simplified by adding some pure ferrous sulphate (free from ferric iron) and potassium sulphocyanide to the copper solution and titrating direct with the vanadous sulphate.

TABLE III.

Strenght of vanadous sulphate = 0·776N/10. 1 C. c. = 0·004898g. Cu

Vol of Cu^{++} soln.	Vol of V^{++} soln.	Amount of Cu found.	Remarks.
10 c.c.	7·3 c.c.	100·06%	Titrations carried out in presence of 1c. c. of pure ferrous ammonium sulphate soln.
10	7·3	100·06	
20	14·6	100·06	
10	13·4	100·06	Titrations made after the addition of 5c. c. of ferric alum soln. 5C.c. ferric alum soln. = 6·1c.c V^{++} soln.
10	13·4	100·06	
20	20·7c.c.	100·06	

Copper was also estimated from the solution by electrolytic and iodometric methods ; the former method gave 100·3% Cu and the latter 99·93% Cu.

Estimation of Chromium.

For the determination of chromium the chromic salts must be converted into chromic acid. This was effected by oxidising the chromic salt with sodium peroxide, boiling off the excess of oxygen

and then neutralising with sulphuric acid. After cooling the solution in a conical flask, an excess of vanadous sulphate was run into the mixture. The excess of vanadous salt was then titrated back with the standard ferric alum solution using potassium sulphocyanide as an indicator. It is necessary to note here that potassium sulphocyanide should not be added until all the chromic acid has been reduced, because chromic acid acts upon ferric sulphocyanide producing persulphocyanogen. (*cf.* Knecht and Hibbert, "Volumetric Analysis".)

Pure potassium dichromate (2·4895 g.) was dissolved in water and the solution was made up to 500 c. c. A known volume of this solution was reduced with an excess of vanadous sulphate which was then titrated back with the standard ferric alum solution.

TABLE IV.

Vanadous sulphate soln. = 1·48N/10. Ferric alum soln. = 0·9472N/10

Vol of dichromate soln.	Vol. of vanadous soln.	Vol of Fe^{+++} soln.	Amount of chromium Found.	Present.
10 c.c.	10 c.c	4·85c.c.	0·01769g.	
10	10	4·90	0·01761	0·01760g.
10	10	4·90	0·01761	

In conclusion, my best thanks are due to Mr. R. L. De, M. Sc. for his kind interest during the progress of this work.

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Volumetric Estimation of Chlorides and Sulphates in a Mixture Containing both, with the Help of an Adsorption Indicator.

By M. B. Rane and K. R. Apte.

The use of dyestuffs as what Kolthoff calls 'adsorption indicators' in volumetric analysis, is of recent origin. Various methods have been suggested for the estimation of Cl, Br, I, Ag, (Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495) oxalates (Wellings, *Trans. Faraday Soc.*, 1932, **28**, 565), volumetrically with the help of adsorption indicators.

During recent times Wellings (*Trans. Faraday Soc.*, 1932, **28**, 561) suggested a method for estimation of sulphates volumetrically using fluorescein as an adsorption indicator. The authors have tested the method and found it quite satisfactory, though it must be admitted that a good deal of practice is needed to enable one to judge the end-point correctly. The scope of Wellings' method is, however, very limited as good results are not obtained in presence of chlorides, nitrate and free acids. In the present paper the authors have found out a method not only of eliminating the interference caused by the presence of chlorides in the estimation of sulphates but they have developed a method of estimating volumetrically both the chloride and the sulphate one after the other in the same solution.

It is also found that the sulphate can be estimated even in the presence of free acid (HCl and acetic), provided the free acid is just neutralised by dilute ammonia, the excess of ammonia being boiled off, before titrating the solution against standard baryta. It has, however, not been found possible to get over the interference caused by nitrates and nitric acid.

Since the authors found by experiments that the presence of free acetate (CH_3COO') ions does not interfere in the titration of sulphate by barium hydroxide, a solution of CH_3COOAg is added to a solution containing the chloride and sulphate till all the chloride ions are precipitated. After this the sulphate is easily estimated by Wellings' method. The precipitated AgCl does not in any way interfere.

The next step was to estimate the amount of chloride first by using a standard solution of silver acetate with fluorescein indicator which changes colour from white to brick red. After the estimation of chloride, the same solution containing the precipitated AgCl, is titrated further against standard baryta solution, the indicator fluorescein present in the solution now changing colour from yellow—pink—orange, when the sulphate is completely precipitated. The amount of chloride can be calculated from the volume of the standard silver acetate solution used, while the volume of the baryta required gives the amount of SO_4'' in solution.

Mixtures containing, (1) $MgSO_4$, $7H_2O$ and KCl; (2) $MgSO_4$, $7H_2O$ and NaCl; (3) Na_2SO_4 and NaCl; (4) K_2SO_4 and KCl; (5) $(NH_4)_2SO_4$ and KCl and (6) $3CdSO_4$, $8H_2O$ and KCl were estimated by the method given above volumetrically and quantitative results were obtained showing that the sulphates and the chlorides when present together can be estimated volumetrically one after the other.

Mixtures containing the various sulphates acidified with varying but known quantities of HCl were taken. The acid was neutralised by dilute ammonia and Cl′ ion precipitated with silver acetate. The solution on titration with $Ba(OH)_2$ gave quantitative results for the SO_4'' present in the solution.

Experimental.

(A) A solution of baryta was prepared and standardised from time to time by $M/10$-succinic acid, prepared from Merck's analytical reagent.

(B) The following solutions were prepared from pure reagents, the strength in each case was confirmed by the estimation of SO_4 gravimetrically as $BaSO_4$ and also volumetrically by the method of Wellings.

$M/10$-$MgSO_4$. $7H_2O$	...	24·60 g./litre.
$M/10$-Na_2SO_4	...	14·20
$M/10$-K_2SO_4	...	17·40
$M/10$-$(NH_4)_2$ SO_4	...	13·20
$3CdSO_4$, $8H_2O$	...	19·23

(C) The solutions of the following chlorides were prepared from Merck's analytical reagents.

N/20-NaCl	2·925 g. in a litre.
N/20-KCl	3·725 ,, ,,

(D) Pure silver acetate was prepared from $AgNO_3$ first by precipitation of Ag as carbonate and subsequently dissolving in glacial acetic acid and recrystallising. The solution of silver acetate was standardised by standard thiocyanate (Volhard's method and also by standard KCl solution, Mohr's method). The strength of the solution used was 7·5910 g./litre.

(E) Fluorescein indicator : 1 G. of fluorescein was dissolved by boiling it with 50 c.c. of rectified spirit and making up the solution to 100 c.c. with the same solvent. All solutions were prepared in CO_2 free distilled water.

Different sulphates (25c.c. to 50 c.c.) were taken to which varying amounts of different chlorides from 1 c.c. to 30c.c. were added. The mixtures were first titrated against standard silver acetate for the chloride and then against standard baryta for the sulphate. 5 C.c. of 5% solution of magnesium acetate were added in each case, (excepting in the case of magnesium sulphate), before titrating it with baryta solution, because the colour change with fluorescein occurs only on the colloidal particles of magnesium and manganese hydroxide and not on the $BaSO_4$ (*cf. Trans. Faraday Soc.*, 1932, **23**, 563). It was also found that cadmium sulphate solution could also be titrated against $Ba(OH)_2$ like magnesium and manganese sulphate, *i.e.*, it did not require the addition of any magnesium acetate.

From the numerous experiments that were performed with mixtures containing the sulphates mentioned above and alkali chlorides, it was found that the volume of the silver acetate required for the titration of the chloride in the mixture, was exactly the same as that required for the calculated quantity of the chloride present in the mixture, and the sulphate could be estimated in the mixture within an error of 0·4%.

The results obtained by titration are summarised in the table given below :

Mixture of chloride and sulphate (c.c.).	Ag-acetate.	$Ba(OH)_2$.	Chloride per litre.		Sulphate per litre.	
			Expt.	Theo.	Expt.	Theo.
4·0 KCl + 25·0 $MgSO_4$	4·40c.c.	26·10 c.c.	3·725g·	3·725g.	24·69g.	24·60g.
15·0 ,, + 30·0 ,,	16·50	31·30	,,	,,	,,	,,
30·0 ,, + 50·0 ,,	33·00	52·20	,,	,,	,,	,,
5·0 NaCl + 25·0 $MgSO_4$	5·50	26·10	2·93	2·91	,,	,,
20·0 ,, + 40·0 ,,	22·00	41·70	,,	,,	,,	,,
4·0 NaCl + 25·00 Na_2SO_4	4·40	26·10	2·93	2·94	14·25	14·20
15·0 ,, + 30·0 ,,	16·50	31·30	,,	,,	,,	,,
9·0 KCl + 25· Na_2SO_4	9·90	26·10	3·725	3·725	17·33	17·40
30·0 ,, + 50·0 ,,	33·00	52·20	,,	,,	,,	,,
15·0 ,, + 30·0 $CdSO_4$	16·50	23·40	3·725	3·725	19·22	19·23
20·0 ,, + 40·0 ,,	22·00	29·20	,,	,,	,,	,,

Summary.

1. The sulphate in the solution can be volumetrically estimated by a standard solution of baryta even in the presence of a chloride.

2. The chloride and the sulphate in a mixture can be estimated volumetrically one after the other by silver acetate and baryta respectively, fluorescein serving as an adsorption indicator for both.

3. The sulphate can be estimated by baryta by the method suggested in this paper even in the presence of HCl and CH_3COOH provided the acid is neutralised by ammonia before titration.

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Review.

Einleitung in das Studium der Chemie, Remsen-Reihlen. 9 Vollig neubearbeitete Auflage. Von Professor Dr. Hans Reihlen. Verlag Von Theodor Steinkopff. Dresden und Leipzig. 1935, pp. 317.

The book is essentially a new one. Professor Reihlen refers to the popularity in Germany of American books which place the readers' standpoint in the forefront. The American student has to spend a considerable amount of his time in athletics and in instructions designed to fit him for modern citizenship. He has also to learn a large number of subjects. The author has therefore addressed himself to a simplification of the course to suit modern tendencies and requirements but not at the expense of clarity of exposition, or of essential facts. Chemical calculations, technical aspects and fundamentals of modern theoretical chemistry have been sufficiently discussed in so far as they are absolutely dispensable. In the opinion of the author, the atomic and ionic theories and the conception of chemical equilibrium are indispensable for a comprehension of the basic facts. The theoretical principles have everywhere been introduced with reference to experiments and the deductive and descriptive methods have been followed in preference to lengthy inductive reasonings which are more likely to confound the beginner.

The book covers practically the course corresponding to the Intermediate standard of Indian Universities but contains more information in some respects than is available in the usual text books. The first chapter deals with chemical processes, energy forms, nature of chemical reactions, distinction between elements, compounds and mixtures, equations and formulæ and also contains a few lines on the distribution of elements in the earth's crust. The successive twelve chapters follow more or less the usual arrangement. Detailed instructions regarding the manner of carrying out experiments have been purposely avoided. The diagrams and the descriptions given are however sufficient for most purposes. Structural formulæ have been given and discussed quite frequently. A short section has been devoted to isomorphism and colloids. Explosives and substances

used in chemical warfare, *e.g.*, poison gases and measures of protection have been dealt with more fully than is usual with books having the same scope. Radio-activity and the Rutherford-Bohr atom find a desirable place. A section is also devoted to the fundamental conceptions of organic chemistry and the structural formulæ of compounds have been given. In the opinion of the reviewer the author has been successful in his main object and books of a similar type will be very helpful for the students of Indian Universities.

J. N. M.

Wachse, Wachsähnliche stoffe und Technische Wachsgemenge (Technische Fortschrittsberichte Bd. XXXI). Von Emil J. Fischer. Verlarg Von Theodor Steinkopff, Dresden und Leipzig. 1934, pp. 122. Price RM. 13.

The book contains a useful collection of materials for those who are desirous of entering into research in the field of waxes. The chapters on synthetic wax, and artificially prepared mixtures of wax-like substances are specially interesting, whilst the best chapter containing a general statement of the uses of waxes and wax-like substances, appears to be quite useful. The book is full of tables from which the point of view of the general reader as also of the investigator, are very important. The treatise should be consulted by all who want to get a real insight into wax technology.

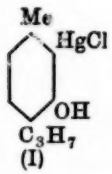
H. K. S.

A New Method of Preparing Organo-mercury Compounds of Phenols and Aromatic Amines. Part II.

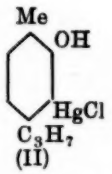
By Panchanan Neogi and (Late) Gopal Krishna Mukherjee.

The method of preparing organo-mercury compounds of phenols and aromatic amines by adding the organic compound to a mixture of sodium bicarbonate and mercuric chloride in the presence of glycerine has already been described (Neogi and Chatterji, *J. Indian Chem. Soc.*, 1928, **5**, 221). The phenol-mercury compounds described there, are, however, oxymercurichlorides, excepting in the case of phenol itself. In the present paper organo-mercury compounds of naphthols, thymol, carvacrol, nitrophenols, 8-oxyquinoline and several aromatic amines and nitroamines have been described which have been prepared following practically the same method. It is to be noted, however, that in the case of naphthols, thymol, carvacrol, and nitrophenols the HgCl radical is attached to the nucleus leaving the hydroxyl group free. The compounds readily dissolve in dilute alkalis without decomposition and readily couple with diazotised β-naphthylamine giving brilliant azo dyes which contain mercury.

It is well known that coupling always takes place in the *para*-position to the hydroxyl group in preference to the *ortho*-position and when the *para*-position is occupied by mercury, the mercury atom is eliminated (Bamberger, *Ber.*, 1898, **31**, 2624). The following structures are, therefore, assigned to the mercurated thymol (I) and carvacrol (II).

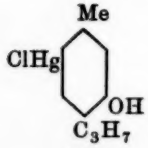


(I)



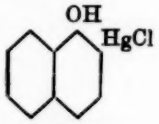
(II)

As thymol-mercurichloride prepared by Dimroth (*Ber.*, 1907, **35**, 2864) by the action of sodium chloride on the acetic acid solution of the product of the reaction of mercuric acetate and thymol differs from our compound, Dimroth's compound has probably the structure (III).



(III)

As substitution in β-naphthol generally takes place in position 1 and as the β-naphthol-mercurichloride described in this paper retains the HgCl group even after coupling with diazotised β-naphthylamine, it is evident that the HgCl group is not in position-1. The constitution of α-naphthol-mercurichloride should, however, be (IV) as α-naphthol generally couples in the *para*-position to the hydroxyl group which thus remains free.



(IV)

It is interesting to note that in the case of nitrophenols only the *o*- and *p*-nitrophenols can be mercurated in this way, whereas the *m*-nitrophenol cannot be mercurated even when the reactants are left together for several days. In the case of 8-oxyquinoline, however, the mercury compound obtained is an oxymercuri derivative, since it is insoluble in dilute alkalis and is decomposed by hot alkalis and H_2S.

The mercurated amines prepared by this method have been purified by shaking with a saturated solution of sodium chloride followed by absolute alcohol which dissolves the additive compound of amine with mercuric chloride and also any precipitated oxychloride of mercury. Nitroamines do not form additive compounds with mercuric chloride. The mercury compounds of aromatic amines and nitroamines are N-Hg compounds with the HgCl attached to the nitrogen atom, as all the compounds are yellow or red and all of them are decomposed at once by dilute solutions of alkalis as also by H_2S.

Experimental.

Phenols.

β-Naphthol-mercurichloride.—To a solution of β-naphthol (4·3 g.) in 50% alcohol, glycerol (15 c. c.) was added and then a solution of

mercuric chloride (8·1 g.) in 50% alcohol when no precipitate appeared. To the mixture an aqueous alcoholic solution of sodium bicarbonate (2·5 g.) was added and vigorously shaken, when a yellowish white precipitate appeared and profuse evolution of carbon dioxide took place. The whole was allowed to rest for several hours and then filtered and washed with a very dilute solution of hydrochloric acid and water. It was finally crystallised from alcohol as needles, m. p. 180° (decomp.). It is insoluble in dilute acids but readily soluble in dilute caustic soda or caustic potash solution. It is decomposed by strong hydrochloric acid or H_2S. (Found: Hg, 53·03. $C_{10}H_7OClHg$ requires Hg, 52·83 per cent).

β-Naphthylazochloromercuri-β-naphthol.—β-Naphthylamine (1 mol.) was diazotised and to the diazonium salt was added a solution of β-naphthol-mercurichloride in dilute caustic soda and briskly stirred. The whole was then kept in ice for several hours after which the alkaline solution was filtered off and the filtrate acidified with acetic acid when the azo-dye was precipitated. It dissolved in hot alcohol from which it was obtained on cooling as a chocolate brown powder, m.p. 170° (decomp.) It insoluble in dilute acids. Strong acids decompose it as also H_2S. It is readily soluble in dilute alkalis giving a red solution. (Found: N, 5·41; Hg, 37·7. $C_{20}H_{13}ON_2ClHg$ requires N, 5·26; Hg, 37·56 per cent).

α-Naphthol-2-mercurichloride was prepared in exactly the same way as the β-naphthol compound. It was obtained as a light grey powder insoluble in alcohol or other common organic solvents but soluble in dilute alkalis. Strong acids as also H_2S decompose it. When heated it at first turns grey at 175° and finally melts at 205° (decomp.). (Found: Hg, 53·10. $C_{10}H_7OClHg$ requires Hg, 52·84 per cent).

4-β-Naphthylazo-2-chloromercuri-α-naphthol was prepared by the action of alkaline solution of α-naphthol-2-mercurichloride on diazotised β-naphthylamine. It was obtained as a chocolate powder insoluble in alcohol or in other common organic solvents but soluble in dilute alkalis giving a chocolate-red solution. On heating it turns grey at 130° and completely decomposes at 180°. It is decomposed by strong acids and by H_2S. (Found: N, 5·5; Hg, 37·75. $C_{20}H_{13}ON_2ClHg$ requires N, 5·26; Hg, 37·56 per cent).

Carvacrol-3-mercurichloride crystallised from alcohol as colourless silky needles melting at 182° (decomp.). It is readily soluble in dilute

alkalis and is decomposed by strong acids and by H_2S. (Found: Hg, 52·20. $C_{10}H_{13}OClHg$ requires Hg, 52·01 per cent).

5-*β-Naphthylazo*-3-*chloromercuricarvacrol* is soluble in hot alcohol from which it separates as a brown powder decomposing at 160°. It is insoluble in dilute acids but dissolves in dilute alkalis giving a reddish yellow solution. It is decomposed by strong acids and by H_2S. (Found: N, 5·4; Hg, 37·30. $C_{20}H_{19}ON_2ClHg$ requires N, 5·2 ; Hg, 37·15 per cent).

Thymol-2-*mercurichloride* was obtained as a white powder which dissolved in hot alcohol from which it appeared on cooling as small needles melting with decomposition at 160°. It is insoluble in dilute acids but readily soluble in dilute alkalis whereas strong acids and H_2S decompose it at once. (Found: Hg, 52·37. $C_{10}H_{13}OClHg$ requires Hg, 52·01 per cent).

6-*β-Naphthylazo*-2-*chloromercurithymol*, prepared from thymol-2-mercurichloride and diazotised β-naphthylamine, is a brown powder insoluble in alcohol or other common organic solvents decomposing at 195°. It is insoluble in acids but soluble in dilute alkalis giving a brown solution. (Found : N, 4·95 ; Hg, 37·40. $C_{20}H_{19}ON_2ClHg$ requires N, 5·2 ; Hg, 37·15 per cent).

2-*Nitro*-6 (?)-*chloromercuriphenol*.—It was obtained as a yellow powder which crystallised from alcohol as light yellow needles, m. p. 185° (decomp.). It is insoluble in acids but readily dissolves in dilute alkalis giving an intense yellow solution. (Found: N, 3·90 ; Hg, 53·81. $C_6H_4O_3NClHg$ requires N, 3·75 ; Hg, 53·55 per cent).

Quinoline-8-*oxymercurichloride* was obtained as a reddish yellow powder, insoluble in common organic solvents as also in dilute alkalis but dissolves readily in dilute hydrochloric acid. It is readily decomposed by caustic soda solution on slight heating as also by H_2S. It decomposes at 205°. (Found: N, 3·66 ; Hg, 52·90. $C_9H_6ONClHg$ requries N, 3·69 ; Hg, 52·7 per cent).

4-*Nitro*-2 (or 6)-*chloromercuriphenol* was obtained as a yellow powder which crystallised from hot alcohol as light yellow needles, m.p. 180° (decomp.). It is insoluble in dilute acids but readily dissolves in dilute alkalis giving an intense yellow solution. (Found: N, 3·90 ; Hg, 53·91. $C_6H_4O_3NClHg$ requires N, 3·75 ; Hg, 53·55 per cent).

Aromatic Amines and Nitroamines.

α-*Naphthylamine-mercurichloride* was obtained as a yellow powder insoluble in common organic solvents but readily soluble in mineral

acids. It decomposes at 125°. It is readily decomposed by H_2S. (Found: N, 3·5 ; Hg, 53·20. $C_{10}H_8NClHg$ requires N, 3·70 ; Hg, 52·92 per cent).

β-Naphthylamine-mercurichloride was obtained as a yellow amorphous powder turning red at 120° and melting with decomposition at 170°. It is insoluble in common organic solvents but soluble in dilute mineral acids. It is readily decomposed by H_2S. (Found: N, 3·9 ; Hg, 52·70. $C_{10}H_8NClHg$ requires N, 3·70 ; Hg, 52·92 per cent).

2-*Methylphenyl*-1-*aminomercurichloride*, prepared from *o*-toluidine, is a deep yellow powder decomposing at 165°, insoluble in common organic solvents but soluble in dilute mineral acids. It is readily decomposed by H_2S. (Found: N, 3·90 ; Hg, 58·18. C_7H_8NClHg requires N, 4·10 ; Hg, 58·56 per cent).

3-*Methylphenyl*-1-*aminomercurichloride*, prepared from *m*-toluidine, is a light yellow powder decomposing at 180°. (Found: N, 4·22; Hg, 58·68. C_7H_8NClHg requires N, 4·10 ; Hg. 58·56 per cent).

4-*Methylphenyl*-1-*aminomercurichloride*, obtained from *p*-toluidine, is a yellowish white powder decomposing at 130°, (Found: N, 4·31 ; Hg, 58·90. C_7H_8NClHg requires N, 4·10 ; Hg, 58·56 per cent).

Dimethylphenylamine-mercurichloride, prepared from xylidine, is a deep yellow powder decomposing at 115°. (Found: N, 3·75 ; Hg, 56·65. $C_8H_{10}NClHg$ requires N, 3·94 ; Hg, 56·26 per cent).

2-*Nitrophenylamine-mercurichloride* was obtained as a scarlet-red powder decomposing at 240°. (Found: N, 7·25; Hg, 54·02. $C_6H_5O_2N_2ClHg$ requires N, 7·52 ; Hg, 53·70 per cent).

4-*Nitrophenylamine-mercurichloride*, prepared from *p*-nitroaniline, is a red powder decomposing at 225°. (Found: N, 7·68 ; Hg, 53·42. $C_6H_5O_2N_2ClHg$ requires N, 7·52 ; Hg, 53·70 per cent).

3-*Nitrophenylamine-mercurichloride*, obtained from *m*-nitroaniline, is a yellow powder decomposing at 140°. (Found: N, 7·91 ; Hg, 53·50. $C_6H_5O_2N_2ClHg$ requires N, 7·52; Hg, 53·70 per cent).

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The "Electron Transfer" Theory Applied to the Reactions in the (Photographic) Developing Bath.

By K. Madhusudanan Pandalai.

In a previous paper it was shown (Pandalai and Rao, *Z. anorg. Chem.*, 1933, **215**, 23) that sodium sulphite besides acting as a preservative for developing solutions, preventing the atmospheric oxidation of the organic reducing agent, and also preventing yellow or brown stains on the negatives, also regenerates the oxidised developing agent enabling the latter to reduce more than its equivalent of the silver halide. The object of this paper is to show that the essential reactions occurring in the developing bath conform to typical reactions of "reduction" in the modern conception of the term, by an application of the "electron transfer" theory of oxidation-reduction processes. This theory regards the essential oxidation-reduction processes as a transfer of electrons from the reducer to the oxidiser. While it is convenient for describing the oxidation and reduction of ionised systems such as inorganic salts, *e.g.*,

$$Fe^{\oplus\oplus} \rightleftharpoons Fe^{\oplus\oplus\oplus} + \ominus$$

it is less convenient for expressing the same *mutatis mutandis* of organic substances as their ionisations have to be taken into consideration. But our knowledge about the nature of these organic reducers in solution is still obscure and superficial. If we put (A) for the reducing agent and (B) for the substance reduced, typical reduction reactions may be expressed as

$$AH_2 + B \longrightarrow A + BH_2 \quad \ldots \quad (i)$$

in which a gain of hydrogen atoms takes place; the reducer being the hydrogen donator and the reduced substance, the hydrogen acceptor.

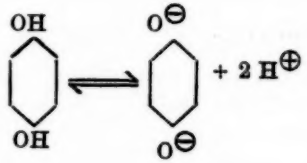
$$A^{\ominus\ominus} + B \longrightarrow A + B^{\ominus\ominus} \quad \ldots \quad (ii)$$

In (*ii*) the anions of the reducer (A), reduce (B) by transferring to it the electron pair or the same as (B) gaining negative charges.

$$B^{\oplus} + A \longrightarrow A^{\oplus} + B \qquad \ldots \qquad (iii)$$

In (*iii*) the reducer (A) abstracts away a positive charge from the substance reduced (B), in other words (B) suffers a loss of positive charge.

These general ideas fit in, in a very significant manner to the reactions taking place during the development of a photographic plate, in other words, in the reduction of the silver halides by the organic reducing agents in presence of sodium sulphite. Most of the organic developing agents are substances containing hydrogen atoms which they can easily part with. These hydrogen atoms are in a large number of cases acidic in character. Thus hydroquinone for example ionises in solution:



In a few cases, however, they exhibit no acidic character and in such cases the theory in this form becomes somewhat artificial. The theory nevertheless has a very wide application.

The first reaction occurring in the developing bath is the ionisation in presence of alkali (accelerators) of the organic reducer (developer). Taking hydroquinone for example

$$C_6H_4O_2H_2 \overset{\text{alkali}}{\rightleftharpoons} C_6H_4O_2^{\ominus\ominus} + 2\,H^{\oplus}$$

the anions of the developer immediately lose their charges

$$C_6H_4O_2^{\ominus\ominus} + 2Ag^{\oplus} \longrightarrow C_6H_4O_2 + 2\,Ag.$$

In presence of sodium sulphite the primary oxidation product of the developer undergoes the following changes ultimately regenerating the original developer.

$$C_6H_4O_2 + 2H^{\oplus} + SO_3^{\ominus\ominus} \rightleftharpoons C_6H_4O_2H_2SO_3$$

$$C_6H_4O_2 + C_6H_4O_2H_2SO_3 \rightleftharpoons C_6H_4O_2H_2 + C_6H_4O_2SO_3$$

$$C_6H_4O_2SO_3 + 2H^{\oplus} + SO_3^{\ominus\ominus} \rightleftharpoons C_6H_4O_2H_2(SO_3)_2$$

$$C_6H_4O_2H_2\,(SO_3)_2 + 2\,H_2O \rightleftharpoons C_6H_4O_2H_2 + 2\,H_2SO_4$$

The quinonoid primary oxidation products being unstable in presence of hydroxyl ions, simultaneous reduction and substitution of hydroxyl in another molecule of quinone appears to take place. Referring to the transformation quinone$\rightleftharpoons$hydroquinone, Kehrmann (*Ber.*, 1898, **31**, 979) observed that "the lower the homologue and the more negative the substituents, the more easily quinones take up hydrogen and pass into hydroquinones." It is likely that in the method of Nietzki (*Ber.*, 1886, **19**, 1467) for preparing hydroquinone from quinone and sulphurous acid, the reactions occurring are those tabled above. Dodgson (*J. Chem. Soc.*, 1914, **105**, 2435) has definitely shown that the course of the reaction is

$$C_6H_4O_2 + SO_2 + 2H_2O \longrightarrow C_6H_4(OH)_2 + H_2SO_4.$$

Rzymkowski (*Z. Elektrochem.*, 1925, **31**, 371) has used thiosulphate as a reducing agent in the determination of quinone (and quinhydrone) and the reactions here, are analogous to those taking place between quinone and sulphite ions.

The most important development reaction is the reduction of ionic into metallic silver. Tubandt (*Z. anorg. Chem.*, 1920, **110**, 196; 1921, **115**, 105) has studied the mechanism of transport of electricity through "solid electrolytic conductors" and has shown that in the halides of silver, the process of conductance is analogous to that in solutions. In the photographic plate the source of silver (being an emulsion of silver halide) the observation of Tubandt is very significant. Further, Hurter and Driffield (E. Thorpe, "Dictionary of Applied Chemistry," 1924, Vol. 5, p. 208) have shown that when the reducer diffuses into the emulsion film and reaches the silver halide grains, the silver salt passes into solution and is ionised, reduction then occurring. Taking hydroquinone as a typical example the essential reactions are represented as below.

(*a*) $C_6H_4O_2H_2 \longrightarrow C_6H_4O_2^{\ominus\ominus} + 2\,H^{\oplus}$

(*b*) $C_6H_4O_2^{\ominus\ominus} + 2Ag^{\oplus} \longrightarrow C_6H_4O_2 + 2Ag$

(*c*) $C_6H_4O_2 + SO_3^{\ominus\ominus} + H_2O \longrightarrow C_6H_4O_2H_2 + SO_4^{\ominus\ominus}$

(*d*) $Ag\ Halide \longrightarrow Ag^{\oplus} + Halide^{\ominus}$

(*e*) $2Ag^{\oplus} + SO_3^{\ominus\ominus} + H_2O \longrightarrow 2Ag + H_2SO_4$

Reaction (*a*) involves the ionisation of the organic reducer in presence of a suitable medium giving rise to reactive hydrogen ions which are extremely powerful reducers. This reaction is also brought about by the well known oxidising action of silver halides on the organic developers. In reaction (*b*) part of development occurs, when the silver ions attain electroneutrality. Reactions (*c*) and (*e*) are typical hydrolytic oxidation-reduction reactions where sodium sulphite plays the most important part. It acts as a stain preventive preservative, and more important of both as hydrogen acceptor with a dual rôle, since in two hydrolytic oxidation-reduction reactions it regenerates the original developer (*vide c*) and reduces an amount of the silver ions (*vide e*) by abstracting away their positive charges. The silver formed in (*b*) and in (*e*) in solution, soon becomes saturated and equilibrium is attained. The organic developers function as hydrogen donators (*vide a*) and inductors (*vide c*) which is the secondary reaction and which is induced by the primary reaction namely the oxidation of the easily oxidisable substances such as hydroquinone, pyrogallol, metol, etc.

My thanks are due to Mr. G Gopala Rao, M.Sc., A.I.C., for helpful criticisms.

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Studies On Optical Activity and Chemical Constitution. Part I. Optically Active Bases and Acids.

BY MAHAN SINGH.

Phenylenebisiminocamphor (I) (Forster and Thornley, *J. Chem. Soc.*, 1909, **95**, 942), 1 : 4 naphthylenebisiminocamphor (II) (Singh and Singh, *ibid.*, 1920, **117**, 1599), camphorylaminophenyliminocamphor (III) (Forster and Saville, *ibid.*, 1921, **119**, 789) and *pp'*- diphenylaminobisiminocamphor (IV) (Singh, Singh and Lal, *ibid.*, 1921, **119**, 1971) are examples of substances possessing very high rotatory powers. All of them contain an optimum association of azethenoid groups, conjugated linkages and a benzene or a naphthalene ring within a narrow

molecular compass. Working on these lines, Patel and Guha (*J. Indian Chem. Soc.*, 1934, **11**, 87) have prepared 1:4-naphthylenebisiminobenzylideneiminocamphor (V) which has a remarkably high rotatory power $[\alpha]^{25}_{5780} = 3340{\cdot}9°$ (pyridine).

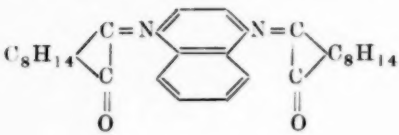
This paper describes the condensation products of camphorquinone and *m*- and *p*-aminodimethylanilines. *p*-Dimethylaminophenyliminocamphor (VI) is endowed with very high specific rotatory powers even though it does not possess the essentials of the above-mentioned compounds. The following table records the rotatory powers of the above compounds together with the rotatory powers of *p*-dimethylaminophenyliminocamphor.

TABLE I.

I. 1:4-Phenylenebisiminocamphor

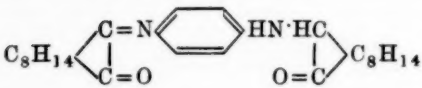
$[\alpha]_D = 1509°$ ($CHCl_3$)

II. 1:4-Naphthylenebisiminocamphor



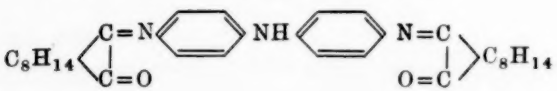
$[\alpha]_D = 1797°$

III. Camphorylaminophenyliminocamphor



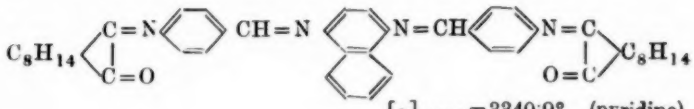
$[\alpha]_D = 1641°$

IV. *pp'*-Diphenylaminobisiminocamphor



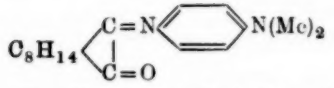
$[\alpha]_D = 2300°$ ($CHCl_3$)

V. 1:4-Naphthylenebisiminobenzylideneiminocamphor



$[\alpha]_{5780} = 3340{\cdot}9°$ (pyridine)

VI. *p*-Dimethylaminophenyliminocamphor.



$[\alpha]_D = 3000°$ (aniline)

$[\alpha]_{5780} = 3344°$ (aniline)

It will be seen that the rotatory power of *p*-dimethylaminophenyliminocamphor exceeds those of all other compounds. The effect of the $N(Me)_2$ group is thus remarkable. The derivatives of phenyliminocamphor with their rotatory powers have been described by Forster and Thornley (*loc. cit.*) and Singh and co-workers (*J. Chem. Soc.*, 1919, **115**, 566). The values of *p*-derivatives are given below:

$[\alpha]_D$ (chloroform).

$-COOH$	$-Br$	$-Cl$	$-H$	$-Me$	$-OMe$	$-OEt$	$-OH$	$-N(Me)_2$
423°	534°	642°	726°	854°	1223°	1250°	1363°	2357°

The $N(Me)_2$ group has raised the rotation of phenyliminocamphor to a considerable extent. A similar effect of the $N(Me)_2$ group has been recorded by Betti (*Gazzetta*, 1923, **53**, 424). He has condensed *d*-β-naphtholbenzylamine with benzaldehyde and substituted benzaldehydes. The rotatory powers of the original base, the condensation product with benzaldehyde and dimethylamino derivative are given below:—

$R-NH_2$	$R{\cdot}N=CH{\cdot}C_6H_5$	$R{\cdot}N:CH-C_6H_4-N(Me)_2$
$[M]_D = 146{\cdot}6°$	$[M]_D = 373°$	$[M]_D = 2676°$

where $R = C_6H_5-CH(C_{10}H_6(OH))-$

The introduction of the dimethylamino group in the *p*-position has raised the rotation from $[M]_D = 373°$ to $[M]_D = 2676°$. Here the activity of the free parent amine is regarded as being governed by the amino group which is attached directly to the asymmetric atom. This is an electron repelling group; its optical influence is, therefore, increased by the introduction of another group of the same character, such as $N(Me)_2$.

Rule and co-workers (*J. Chem. Soc.*, 1918, 178; 1929, 2277) in the case of *p*-substituted octyl benzoates have also observed that the $N(Me)_2$ and NH_2 groups give exaltation of rotation. In this case the increase in $[M]_{5461}$ is from $-92°$ to $-163°$ and $-231°$ respectively.

It is commonly known that the rotations of acids and bases often diminish in magnitude or become reversed in sign when the compounds are ionised. This is very marked if the basic group is the only group of high polar character in the molecule.

Many cases of such a fall in the rotatory power are recorded in literature. Among these may be mentioned *d*-amylamine, *l*-nicotine, conine and 1:4′-amino-4-methyldiphenylsulphoxide, all of which undergo a reversal of sign of rotation in hydrochloric acid solution.

When a drop of methyl iodide was added to an alcoholic solution and kept overnight, the rotatory power fell from $[\alpha]_D = 2487°$ to $[\alpha]_D = 1973°$. This may be attributed to the ionisation of the methiodide compound formed.

p-Dimethylaminophenyliminocamphor was examined in benzaldehyde. It has $[\alpha]_D = 1924°$, an exceptionally low figure when compared with the values obtained in other solvents. This value fell to $[\alpha]_D = 1471°$, and the colour of the solution changed from deep yellow to light greenish yellow. A fresh solution in benzaldehyde was examined and gave $[\alpha]_D = 1429°$, which after three days fell to $[\alpha]_D = 304°$. The maximum rotation is obtained with benzaldehyde from freshly opened bottle. This value could not be repeated. The rapid fall of value in the first solution and the successive fresh solutions can be explained by the fact that benzaldehyde is partially oxidised to benzoic acid, which forms a salt with the basic substance.

The rotatory power of *m*-dimethylaminophenyliminocamphor is considerably lower than that of the *para* isomer. The rotatory powers of some *meta* derivatives of phenyliminocamphor are given below:

$[\alpha]_D$ (chloroform).

-Br	-Cl	-COOH	-OH	$-N(Me)_2$	-H
418°	499°	470°	630°	662°	726°

Although the value for the dimethylamino compound is lower than the unsubstituted compound, it is greater than that of any other compound.

Effect of Solvent.

The ideal conditions to study solvent influences are best observed with optically active compounds of simple molecular structure with a strongly polar group situated near the asymmetric carbon atom. The compound under observation certainly contains a strongly polar group $N(Me)_2$, but is not simple in structure.

The dimethylamino derivatives of phenyliminocamphor have been examined polarimetrically in twelve solvents and, in the case of the *m*-compound, and also in three wave-lengths. It is found that using solvents of the general formula C_6H_5X, the increase in the rotatory power due to the variation of 'X' in the solvent molecule is expressed by

$$NH_2 > NO_2 > I > Br > Cl > H > Me.$$

With the exception of the nitro group, this series corresponds with the one that represents the effect of the substituents when introduced into the optically active molecule.

Solvent.	C_6H_6.	PhMe.	PhCl.	PhBr.	PhI.	$PhNO_2$.	$PhNH_2$.
p-Dimethyl	2461°	2396°	2551°	2786°	2851°	2986°	3000°

It has been observed that the dimethylamino group increases the rotation of phenyliminocamphor to a remarkable extent and it is significant that this effect is maximum in the case of aniline, a solvent which contains a strongly polar NH_2 group. In the case of non-benzenoid solvents the order is $C_5H_5N > CS_2 > C_2H_5OH > CHCl_3 > MeOH$

EXPERIMENTAL.

p-Dimethylaminophenyliminocamphor.—Equimolecular quantities of camphorquinone and *p*-aminodimethylaniline were dissolved in absolute alcohol, a little anhydrous sodium sulphate added, and the solution heated on a water-bath under reflux for 3 hours. After evaporating off the excess of alcohol, the solution was cooled and poured into water. The condensation product settled together with a considerable amount of tarry matter. It was extracted with 50-60% alcohol and recrystallised as a light brown fluffy crystalline mass, m. p. 135·5° after deepening in colour.

The yield did not improve even when the reactant substances were heated dry with a little anhydrous sodium sulphate without alcohol. It was readily soluble in methyl or ethyl alcohol, benzene,

carbon disulphide, chloroform and other organic solvents, but insoluble in water.

The substance in alcoholic solution behaves as an indicator similar to methyl orange. It dyes wool yellow. (Found: N, 10·02. $C_{18}H_{24}ON_2$ requires N, 9·86 per cent).

m-*Dimethylaminophenyliminocamphor.*—Molecular proportions of camphorquinone and *m*-aminodimethylaniline in absolute alcoholic solution with a little or no anhydrous sodium sulphate, were refluxed on a water-bath for 3-4 hours. After evaporating off the excess of alcohol, the product was cooled, water added and the whole solution left overnight. The impure product was further twice crystallised from 50% alcohol in beautiful yellow needle-like crystals, melting at 125-26° after changing to a red colour. It is very readily soluble in methyl or ethyl alcohol, benzene, carbon disulphide, etc and soluble in water. (Found: N, 10·1. $C_{18}H_{24}ON_2$ requires N, 9·86 per cent).

Condensation between camphorquinone and *o*-aminodimethylaniline under similar conditions gave a viscous mass which could not be crystallised.

TABLE II.

Specific rotations of p-*dimethylaminophenyliminocamphor.*

Solvent.	Conc.	Temp.	$[\alpha]_D$.
C_6H_6	0·0197 g./25 c.c.	18°	2462
C_6H_5Me	0·0240	18	2396
$C_6H_5NO_2$	0·0252	18	2986
C_6H_5Cl	0·0246	18	2551
C_6H_5Br	0·0245	18	2786
C_6H_5I	0·0253	18	2851
$C_6H_5NH_2$	0·0320	34	3000
C_6H_5CHO	0·0204	19	1924
C_5H_5N	0·0258	19	2791
MeOH	0·0421	20	2352
EtOH	0·0560	22	2487
$CHCl_3$	0·0123	32	2358
CS_2	0·0265	19	2726

The readings for other wave-lengths could not be taken as the solution was too dark.

TABLE III.

Specific rotations of m-*dimethylaminophenyliminocamphor.*

Solvent.	Conc.	Temp.	$[\alpha]_D$.	$[\alpha]_{3780}$.	$[\alpha]_{5461}$.
C_6H_6	0·0417g/25 c.c.	27°	710°	782°	956°
C_6H_5Me	0·0490	27	653	755	944
$C_6H_5NO_2$	0·0488	27	697	790	980
C_6H_5Cl	0·0398	34	647	773	1005
C_6H_5Br	0·0482	27	918	1005	1306
C_6H_5CHO	0·0396	34	568	—	—
C_6H_5CHO	After 27 hours		436	—	—
C_5H_5N	0·0391	27°	723	774	910
MeOH	0·0466	29	628	655	767
$(Me)_2CO$	0·0394	34	584	628	812
CS_2	0·0324	27	756	787	1080
$CHCl_3$	0·0400	32	663	738	963
$C_6H_5NH_2$	0·0488	27	711	793	1003

The author desires to thank Mr. Manohar Singh for the help in taking some of the readings, and Prof. H. B. Dunnicliff, for the facilities he provided and the interest he took during the course of this investigation which is being continued.

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926

On Anacardic Acid. Part I. Anacardic Acid and Tetrahydroanacardic Acid.

By P. Parameswaren Pillay.

Anacardic acid forms about 90% of the corrosive oil of the pericarp of the nut of *Anacardium occidentale*, Linn. This tree (Hindi, *Kaju*; English, *cashewnut*) is an evergreen, 19-20 feet high, growing in the hotter parts of India, especially near the sea. Medicinally, the tarry oil is useful for leprosy, ringworm and obstinate ulcers. It is exported in large quantities from the west coast for use as a raw material in the preparation of synthetic resins and varnishes. Anacardic acid was first separated from the crude oil of the pericarp by Stadeler (*Annalen*, 1847, **63**, 137) by precipitation of the acid from an alcoholic solution of the oil with freshly precipitated lead hydroxide, and decomposing the insoluble lead salt with ammonium sulphide, followed by the liberation of the oil from the ammonium soap by dilute sulphuric acid. Stadeler prepared several metallic derivatives and as the result of many analyses gave it the formula $C_{44}H_{32}O_7$. Ruhemann and Skinner (*J. Chem. Soc.*, 1887, **51**. 663; *Ber.*, 1887, **20**, 1861) repeated his work and established the formula $C_{22}H_{32}O_3$ for the acid. They also prepared a methyl ester and suggested that it was probably a hydroxycarboxylic acid.

In the course of the present investigation it was observed that by Stadeler's method of preparation (*loc. cit.*), aqueous solution of the ammonium salt of anacardic acid was so thick and viscous that it was very difficult to filter it from the fine suspension of lead sulphide. An alternative method was, therefore, devised, based on the solubility of the lead salt in ether. This method has been found to be very much quicker and easier, although the product is a little more coloured.

Careful analyses, estimation of silver in the silver salt and molecular weight d terminations support the formula $C_{22}H_{32}O_3$ of Ruhemann and Skinner (*loc. cit.*) The Zerewitneoff method revealed the presence of 2 active hydrogen in the molecule of the acid. Attempts to methylate it by methyl sulphate and alkali or

to acetylate it by boiling with acetic anhydride were unsuccessful. A unique property of anacardic acid must be noted, *viz.*, that when an alcoholic solution of silver nitrate is added to the acid, the silver salt is precipitated immediately as a white powder accompanied by the simultaneous liberation of nitric acid.

Anacardic acid in very dilute alkaline solution is oxidised with extreme case by potassium permanganate and from the oxidation products oxalic acid and oenanthic acids were isolated and indications of the presence of other dicarboxylic acids were also obtained. No cyclic carboxylic acid could be isolated. Again, when oxidised with concentrated nitric acid on the boiling water-bath, a good quantity of oxalic acid was obtained, but here also no nitrocarboxylic acid could be isolated,

The degree of unsaturation of anacardic acid was estimated by titration against bromine in cooled chloroform solution, and showed that it contained two aliphatic double bonds. The acid was hydrogenated in alcoholic solution in the presence of palladised charcoal as catalyst to give a tetrahydroanacardic acid. Derivatives of tetrahydroanacardic acid have been prepared and studied (*vide* experimental).

The material used was obtained from the Malabar coast.

Experimental.

An improved method for the preparation of anacardic acid.—An alcoholic solution of the crude extract was shaken with an excess of freshly precipitated lead hydroxide. The lead precipitate was filtered, washed with alcohol and shaken in an inert atmosphere with ether which dissolved lead anacardate. It was decanted off and repeatedly shaken in an inert atmosphere with dilute hydrochloric acid, then with water, dried and the solvent distilled off. The anacardic acid remained behind as a brown oil. Either benzene or petroleum ether can replace ether but they tend to form emulsions. This ...ethod is very suitable for the preparation of large quantities of the acid. For purifying the acid, it was dissolved in alcohol, neutralised with a slight excss of aqueous ammonia, then aqueous barium chloride solution added till there was a slight cloudiness. The solution was then shaken with some powdered wood charcoal and kept aside. Anacardic acid came down on acidification and dilution as a light brown oil and constitutes nearly 90% of the extract.

The homogencity of the acid.—The acid, thus obtained, was fractioned by means of alcoholic basic lead acetate into four fractions and

the acid recovered from each of these fractions. The two middle fractions had m. p. between 22-25° and the two others solidified indefinitely some degrees lower. On catalytic reduction of each of these fractions the tetrahydroanacardic acid was obtained in nearly quantitative yield, the m. p. ranging from 86-92°. Even the low-melting product, when twice crystallised gave the substance melting at 93° in good yield.

Properties of anacardic acid.—A pure sample of anacardic acid has the following properties: m.p. 23-25°; $d_{30}^{30} = 1{\cdot}0002$; $n_D^{30} = 1{\cdot}5163$. It is a light brown viscous oil soluble in all common organic solvents. [Found: C, 76·6; 76·8; H, 9·5, 9·5; M.W. (in acetone), 367, 358. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·5 per cent. M.W., 344]. It is soluble in dilute ammonia and in $N/10$-NaOH but with higher concentrations of NaOH it gives a white sodium derivative insoluble in water but soluble in alcohol. The silver salt was prepared by adding alcoholic silver nitrate to an alcoholic solution of anacardic acid, washed and dried in *vacuo*. (Found: Ag, 23·68, 23·72. $C_{22}H_{31}O_3Ag$ requires Ag, 23·94 per cent). The number of active hydrogen by the Zerewitenoff method was found to be two. (Found: Active H, 0·65; 2 H requires 0·58 per cent.) The acid gave an intense violet colouration with alcoholic $FeCl_3$, a slight shade bluer than that given by salicylic acid and of the exact tint as that of *o*-cresotic acid.

Esterification and acetylation by the ordinary methods proved unsuccessful, but the silver salt treated in dry ether with ethyl iodide gave an oil which was insoluble in ammonia and which could not be distilled in *vacuo* without decomposition.

Oxidation of anacardic acid with potassium permanganate.—The acid (10 g.) was dissolved in dilute ammonia and the solution diluted with water to 300 c.c. and oxidised by the slow addition of well powdered potassium permanganate (37 g.) with vigorous stirring. The decolourisation was very quick. The product when filtered, acidified and extracted with ether gave 4·8 g. of acids. From the manganese dioxide precipitate by dissolving in sulphurous acid 3·3 g. of acids were obtained. This was further dissolved in dilute ammonia and oxidised with potassium permanganate (12 g.). From the aqueous filtrates collected together, by neutralisation and precipitation with calcium chloride nearly 2g. of calcium oxalate were obtained. From the other acids, by treatment with petroleum ether 1·8 g. of a liquid acid, soluble in this solvent, were obtained which when distilled boiled chiefly between 220-225°. [Found: C, 64·3; H, 10·3; Ag (in Ag salt), 45·1

per cent. $C_7H_{14}O_2$ requires C, 64·6; H, 10·8; Ag (in Ag salt), 45·6 per cent]. It was confirmed as oenanthic acid by preparing the anilide melting at 67°.

The acids insoluble in petrol were fractionated through the calcium salt. One fraction was obtained as solid, m. p. 150°. It could not be obtained crystalline but appeared to behave like a fatty dicarboxylic acid. No ring acid could be isolated.

Oxidation with concentrated nitric acid.—Anacardic acid (10 g.) was treated in small lots with concentrated nitric acid (*d* 1·48, 75 c.c.) so that the vigorous reaction could be checked, and the product twice evaporated down on the water-bath with nitric acid. The residue when washed with 15 c.c. of hot water gave a yellow solution which when evaporated gave oxalic acid (2·7 g.). The liquid acids insoluble in water were not examined in detail as they did not give indications of the presence of a nitro-acid containing phenolic hydroxyl.

Titration of anacardic acid against bromine.—The acid (1·53 g.) in ice-cooled chloroform solution, titrated against bromine in the same solvent took up 1·40 g. of bromine (2 double bonds require 1·42 g.). The course of the addition was followed by means of potassium iodide-starch paper. The tetrabromide was insoluble in petrol and was obtained as a semi-solid, but could not be obtained in a crystalline form.

Catalytic hydrogenation of anacardic acid.—The acid (4 g.) in 50 c.c. of alcohol was added to palladised charcoal which was previously suspended in 50 c.c. of alcohol and shaken in a hydrogen atmosphere till it had ceased to absorb any more hydrogen (522 c.c. at N.T.P. $2H_2$ require 517 c.c. at N. T. P.). It was filtered, water was added and the solution cooled, when the product was precipitated as a white crystalline mass, m.p. 88-90°, yield 4·0 g. It was crystallised once from alcohol and then from benzene and petroleum ether in shining silky needles, m.p. 92·5-93°. The tetrahydroanacardic acid is soluble in the common organic solvents except in glacial acetic acid and petroleum ether and its chemical properties are quite similar to that of anacardic acid. (Found: C, 75·6, 75·8 ; H, 10·5, 10·4. $C_{22}H_{36}O_3$ requires C, 75·9 ; H, 10·4 per cent). The number of active hydrogen found by Zerewitenoff method was 2 (Found: H, 0·52 ; 2H requires 0·57 per cent). A solution of the acid in absolute alcohol was saturated with hydrochloric acid gas when a substance crystallised out in needles, which was found to be not the ester but the original substance. In order to obtain the ester, the acid was converted to the silver salt through the

ammonium salt. (Found: Ag, 23·57, 23·61· $C_{22}H_{35}O_3Ag$ requires Ag, 23·72 per cent).

Methyl tetrahydroanacardate.—The silver salt suspended in dry ether was kept aside for 3 days with excess of methyl iodide. It was filtered, the ether evaporated off and crystallised by cooling an alcoholic solution in ice. It was pressed on a porous plate and recrystallised in flat needles, insoluble in ammonia, m.p. 49°. (Found: C, 76·4; H, 10·4. $C_{23}H_{38}O_3$ requires C, 76·3; H, 10·5 per cent).

Ethyl tetrahydroanacardate was obtained in a similar manner with ethyl iodide as silky needles, m.p. 38°. (Found: C, 76·7; H, 10·5. $C_{24}H_{40}O_3$ requires C, 76·6; H, 10·6 per cent).

As regards the phenolic hydroxyl group of tetrahydroanacardic acid it was found that it resisted the ordinary methods of acetylation, benzoylation and methoxylation.

The acetyl derivative.—The acid (0·5g.) was dissolved in dry pyridine, (3 c.c.), cooled in ice and acetyl chloride (0·3 c.c.) was very cautiously added with shaking. After 10 minutes the mixture was carefully warmed on the water-bath to a clear solution, cooled and diluted with water. The precipitated oil was washed well with water, purified through the ammonium salt, cooled, acidified and the acid obtained was crystallised from alcohol as needles, m.p. 78° which do not give any colouration with alcoholic ferric chloride. (Found: C, 74·0; H, 9·6. $C_{24}H_{38}O_4$ requires C, 73·8; H, 9·7 per cent).

Monobromotetrahydroanacardic acid.—To the tetrahydroanacardic acid (0·5 g.) dissolved in carbon disulphide (5 c.c.) bromine (0·23 g.) was added dissolved in 3 c.c. of the solvent. The mixture was occasionally slightly warmed. There was evolution of HBr and decolourisation of the solution which was evaporated down and the solid crystallised from benzene, m.p, 77°. (Found: Br, 18·3. $C_{22}H_{35}O_3Br$ requires Br, 18·7 per cent).

Oxidation of tetrahydroanacardic acid: Isolation of oxalic acid and palmitic acid.—To tetrahydroanacardic acid (4 g.) dissolved in acetone (300 c.c.) and water (60 c.c.) was added a solution of potassium permanganate (12·5 g.) in acetone (300 c.c.) and water (100 c.c.). The oxidation was completed by warming on the water-bath for 1 hour. The mixture was cooled, filtered, the manganese dioxide precipitate was washed first with a little acetone, then with boiling water, and the acetone distilled off. The aqueous residue was cooled and acidified. It gave an effervescence of carbon dioxide and 1·7 g. of a fatty acid were obtained which melted at 50-53°; recrystallised from

alcohol it melted at 53-55°. It was distilled under reduced pressure and the distillate crystallised thrice from alcohol, when colourless needles were obtained (0·6 g.), m.p. 60-61°; there being no depression on admixture with a sample of pure palmitic acid. (Found: C, 74·9; H, 12·7. $C_{16}H_{32}O_2$ requires C, 75·0; H, 12·5 per cent). The aqueous filtrate showed the presence of oxalic acid.

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On Anacardic Acid. Part II. The Constitution of Tetrahydroanacardic Acid.

BY P. PARAMESWAREN PILLAY.

Another line of investigation which threw more light on the constitution of anacardic acid was based on its behaviour on heating. On heating the acid in an atmosphere of nitrogen to 230° and distilling the product, there was obtained besides undistillable resin, an oil boiling at 215-20°/14mm. in an yield of approximately 25%. The same product was obtained in an yield of 50% when anacardic acid was distilled in *vacuo*. This oil, which is referred to as anacardol, was found by its analysis, behaviour and catalytic reduction to be the simple decarboxylated product of anacardic acid, standing in the same relationship to it as phenol to salicylic acid. It was observed that, once the carboxyl group became eliminated from anacardic acid, the hydroxyl group became easily reactive, but here again it was found to be more advantageous to study it in the saturated product.

Titration against bromine revealed the presence of two double bonds and on catalytic reduction four atoms of hydrogen were quickly taken up (*cf.* Part I) and the same compound was obtained in good yield, when tetrahydroanacardic acid was distilled under reduced pressure. It was found, however, that if tetrahydroanacardic acid is first decarboxylated by prolonged heating at 200-220° at ordinary pressure it gives besides tetrahydroanacardol, about 25% of another product as needles, almost insoluble in alcohol and melting at 49°.

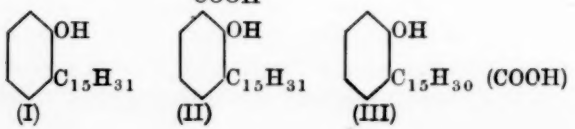
By treatment with alcoholic potash for about 4 hours, it gave a mixture of tetrahydroanacardic acid and tetrahydroanacardol, the components being easily separated by suitable means. This substance, therefore, is tetrahydroanacardyl tetrahydroanacardate and its formation is analogous to the formation of salol by the action of heat on salicylic acid.

Tetrahydroanacardol easily gives crystalline acetyl, benzoyl and phenylurethane derivatives. It was found that distillation under reduced pressure of acetyltetrahydroanacardic acid results in a product melting at 42°, which is found to be the same as tetrahydroanacardyl acetate.

As is the case with other phenols having long fatty side-chains, tetrahydroanacardol gives a solid sodium derivative when rubbed with dilute caustic soda, insoluble in water but soluble in alcohol. It is oxidised by potassium permanganate in acetone solution more easily than tetrahydroanacardic acid with the formation of oxalic and palmitic acids.

The constitution of tetrahydroanacardic acid follows from that of tetrahydroanacardol. The phenolic character of the latter substance is evidenced by its formation from an *o*-phenolic acid by smooth decarboxylation, by the Liebermann's colour reaction, and by the formation of a sodium derivative and of phenols of lower molecular weight by its distillation at ordinary pressure. Since oxidation with potassium permanganate in acetone solution yields palmitic acid, tetrahydroanacardol can be inferred to contain a straight normal side-chain of 15 carbon atoms in its molecule. It is a well known fact observed in the case of saturated fatty aromatic substances that the ring system is easily oxidised with the formation of fatty acids containing one carbon atom more than the side-chain, which remains intact, this carbon atom being derived from the ring. (*cf.* hydrourushiol, hydrolacol, Majima, *Ber.*, 1922, **55**, 172).

Tetrahydroanacardol ($C_{21}H_{36}O$) could, therefore, be written as $OH{\cdot}C_6H_4{\cdot}C_{15}H_{31}$ (n), and since the phenols obtained by the distillation of anacardol under ordinary pressure give salicylic acid by fusion with potash, the side-chain must be in the *ortho* position to the hydroxyl group. Tetrahydroanacardol, therefore, has the structure (I).



(I) (II) (III)

As tetrahydroanacardic acid gives the violet colour reaction with ferric chloride the carboxyl group in the acid must be either in the *ortho*-position to the hydroxyl and attached to the benzene nucleus or attached to the long pentadecyl side-chain *i.e.* the tetrahydroanacardic acid is either (II) or (III).

If the acid has structure (III), oxidation should lead to the formation of a dicarboxylic acid containing 17 carbon atoms in analogy with the final oxidation products of chaulmoogric and hydnocarpic acids, which are dicarboxylic acids containing one carbon atom more than their respective side-chains (Power and Barrowcliff. *J. Chem. Soc.*, 1907, **91**, 557). Tetrahydroanacardic acid gives, however, the monocarboxylic palmitic acid, the carboxyl being evidently formed from the ring carbon atom, the benzene ring being completely ruptured in the process. It follows, therefore, that the carboxyl group of tetrahydroanacardic acid is attached to the benzene nucleus and consequently the acid has the structure (II). The smooth decarboxylation of the acid can be taken as a further evidence of the carboxyl group being attached to the benzene ring, as this appears to be a property common to all the substituted salicylic acids.

It is of interest to note in this connection that from several trees of the *Anacardiaceæ* family, catechol derivatives containing normal side-chains of 15 or 17 carbon atoms have been isolated (Majima and co-workers, *Ber.*, 1922, **55**, 172; Pillay and Siddiqui, *J. Indian Chem. Soc.*, 1931, **8**, 517), so that this kind of fatty aromatic structure seems to be favoured by the *Anacardiaceæ* family of plants.

Experimental.

Action of heat on anacardic acid: Formation of anacardol.—On heating anacardic acid in an atmosphere of nitrogen on the oil-bath, visible evolution of gas above 175° was observed which became quite brisk at 200°. The gas was found to be carbon dioxide. Water too was given off at about this temperature. The residue of brown oil boiled mostly at 215-220° /14 mm. in an yield of about 25%. An yield of about 50% of the samce product was obtained by distilling the anacardic acid under u reded pressure. About half of the anacardic acid taken resinified in the distilling flask to a hard glassy solid insoluble in all the organic solvents and only barely acted on even by boiling nitric acid. The anacardol thus obtained has

the following properties: $d_{30}^{30}=0{\cdot}9399$; $n_D^{30}=1{\cdot}5107$. The substance gives a yellowish green colouration by Leibermann's test for phenols, but is quite insoluble in ordinary caustic soda and does not give any colouration with ferric chloride. It was found to be soluble in exceedingly dilute caustic soda, to a minute degree, much more if about 25% of alcohol was added to it. (Found: C, 84·3; H, 10·6. $C_{21}H_{32}O$ requires C, 84·0; H, 10·7 per cent).

Anacardol (0·584 g.) titrated in ice-cold chloroform solution decolourised 0·58 g. of bromine (two double bonds require 0·62 g. Br). The product was not obtained crystalline.

Catalytic hydrogenation of anacardol: Formation of tetrahydroanacardol.—Anacardol (1·925 g) was hydrogenated in alcoholic solution using palladised charcoal as catalyst. It was very quickly hydrogenated absorbing 298 c c. of H at N. T. P. (2 H_2 require 286 c.c.). Alcohol was distilled off and the product distilled under reduced pressure. The distillate solidified and was crystallised from petroleum ether, m. p. 53-54°. It is very soluble in all the common organic solvents. (Found: C, 83·0; H, 11·7. $C_{21}H_{36}O$ requires C, 82·9; H, 11·8 per cent).

Tetrahydroanacardic acid (1·0 g.) was distilled under reduced pressure, and the product (0·7 g.) which solidified on cooling, was crystallised from petroleum ether, m. p. 54°; the melting point was not lowered by admixture with tetrahydroanacardol obtained by the hydrogenation of anacardol.

The acetyl derivative.—Tetrahydroanacardol (0·2 g.) was boiled with acetic anhydride (1 c.c.) and a drop of pyridine for 2 hours, evaporated on the water-bath and distilled under reduced pressure. The solid distillate was crystallised by cooling an alcoholic solution in ice as needles, m. p. 42°. (Found: C, 79·9; H, 10·9. $C_{23}H_{38}O_2$ requires C, 79·8; H, 11·0 per cent). The same product was also obtained by the distillation under reduced pressure of acetyl tetrahydroanacardic acid.

The benzoyl derivative.—Tetrahydroanacardol (0·3 g.) was heated on the water-bath with an excess of benzoyl chloride for 2 hours, the excess was decomposed with methanol, the product evacuated at 100° for some time, and then the residue distilled under reduced pressure. The distillate, which solidified, was crystallised from hot alcohol as palm-leaf like needles, m. p. 54°. (Found: C, 82·1; H, 9·5. $C_{28}H_{40}O_2$ requires C, 82·3; H, 9·8 per cent).

The phenylcarbamate.—Tetrahydroanacardol (0·2 g.) in petroleum ether (2 c.c.) was treated with phenyl *iso*cyanate (0·15 g.) and kept overnight. It solidified to a white solid which was filtered, washed with petrol and crystallised from alcohol as rosettes of silky white needles, m. p. 79-80°. (Found: N, 3·7. $C_{28}H_{40}O_2N$ requires N, 3·3 per cent).

Oxidation of tetrahydroanacardol: Isolation of palmitic and oxalic acids.—Tetrahydroanacardol (2 g.) dissolved in acetone (70 c.c.) and water (20 c.c.) was oxidised with a solution of potassium permanganate (6 g.) in acetone (80 c.c.) and water (20 c.c.). The reaction mixture became warm and the permanganate was quickly discoloured. It was filtered and worked up as in the oxidation of the acid; it gave besides oxalic acid, 0·8 g. of a fatty acid, m. p. 51-53°. When distilled under reduced pressure and crystallised thrice from alcohol 0·25 g. of an acid was obtained melting at 60-61°, the m. p. was not lowered by admixture with a sample of pure palmitic acid.

Distillation of anacardol under ordinary pressure.—Anacardol (15 g.) was twice distilled under ordinary pressure. Inflammable gases were evolved and the distillate which had a strong phenolic odour was separated by means of caustic soda dissolved in 15% alcohol and shaking with ether into (*a*) phenols (3 g.) and (*b*) non-phenols (7 g.). The latter when distilled over sodium gave what appeared to be hydrocarbons, but with a long range of boiling point. (Found: C, 86·2; H, 13·4 per cent).

(*a*) *Phenols.*—On fractionation, the boiling point of the phenols went on rising from about 200—350°. The first drop gave a violet colour with aqueous ferric chloride.

Potash fusion of phenols.—The phenols (2 g.) were fused with potash (20 g.) and water (4 c.c.) in a nickel crucible. An insoluble sodium salt seemed to be formed which quickly went into solution at about 300°. It was cooled, acidified, extracted with ether and separated by means of sodium bicarbonate into acids and phenols. The acid residue, when taken up with hot water and the water driven out in the desiccator, gave a partially crystalline residue, which was crystallised from hot water as needles (12 mg.) melting at 155 56°. It gives a violet colouration with ferric chloride. The melting point was not lowered by admixture with a sample of salicylic acid. The phenolic fraction (0·3 g.) gave a violet colouration with aqueous ferric chloride and gave with bromine water a bromide, which

crystallised from dilute alcohol in needles melting at 93° and was found to be tribromophenol by mixed melting point.

Action of heat on tetrahydroanacardic acid.—Tetrahydroanacardic acid (2·003 g.) was heated in a current of nitrogen in an oil-bath, and the outgoing gases estimated for carbon dioxide and water. Bubbles of gas began forming at about 195° and the effervescence was quite brisk at 225°. It was heated to 235°. The ebullition stopped in 15 minutes but the heating was continued for another 15 minutes. The substance gave 0·0343 g. of water and 0·1927 g. of carbon dioxide (9·6%; 1 mol. of CO_2 requires 12·6%). The residue was crystallised from alcohol by cooling in ice when 0·6 g. of colourless needles was obtained. This product was almost insoluble in alcohol and melted at 49°. The alcoholic solution precipitated with water gave 1·2 g. of an oil which on distillation was found to be tetrahydroanacardol. The two substances gave a mixed melting point of 40-44° (Found : C, 80·9; H, 11·0. $C_{43}H_{70}O_3$ requires C, 81·4; H, 11·0 per cent).

Sponification of substance melting at 49°.—The substance (0·4 g.) was refluxed on the water-bath with 5 c.c. of 20% alcoholic potash for 4 hours, the alcohol evaporated off, the residue taken up with water and acidified. The product was dissolved in very dilute ammonia (100 c.c.), warmed for some time, cooled and filtered through a wet filter paper. The filtrate on acidification gave an acid (0·16 g.) which was crystallised and identified as tetrahydroanacardic acid. The product in the filter paper was shaken with 100 c.c. of ether, then twice with very dilute ammonia, the ether dried and evaporated off and the residue (0·11 g.) crystallised from petroleum ether. The resulting crystals were found to be tetrahydroanacardol.

I take this opportunity to thank Dr. B. B. Dey of the Presidency College, Madras, and Dr. P. C. Guha of the Indian Institute of Science, Bangalore, for very kindly affording me every facility in their laboratories for carrying on this research.

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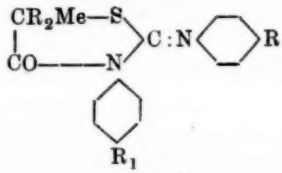
The Formation and Stability of Polybromide Derivatives of Heterocyclic Compounds. Part V. The Bromination of some 2-Arylimino-3-aryl-4-keto-5-methyltetrahydrothiazoles and their 5:5-Dimethyl Homologues and some Remarks on the Theory of Singlet Linkages.

By Bashir Ahmad, Ranchhodji Dajibhai Desai and Robert Fergus Hunter.

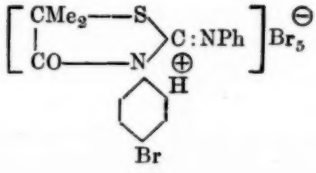
It was assumed in earlier investigations on the bromination of diaryl-ψ-thiohydantoins (Farooq and Hunter, *J. Indian Chem. Soc.*, 1932, **9**, 545; Chowdhury, Desai, Hunter and Solangi, *Rec. trav. chim.*, 1933, **52**, 853), that the keto-enol system

$$CH\ [H]\cdot C:O \rightleftharpoons CH:C\cdot O\ [H]$$

present in these tetrahydrothiazole derivatives takes no part in the production of the bromo-addition compounds formed in chloroform solution at low temperatures. In view of the somewhat curious results observed in the case of 2-*p*-chlorophenylimino-3-*p*-chlorophenyl-4-ketotetrahydrothiazole and its bromine analogue, however, it appeared desirable to test the validity of this assumption by an examination of the behaviour of diaryl-ψ-thiohydantoin derivatives in which one, or both of the potentially mobile hydrogen atoms of the triad system have been alkylated. The bromination of certain 2-arylimino-3-aryl-4-keto-5-methyltetrahydrothiazoles (I, $R_2=H$) and their static 5:5-dimethyl analogues (I, $R_2=Me$) which are readily synthesised from the sodio derivatives of the corresponding *s* diarylthiocarbamides and ethyl α-bromopropionate and ethyl α-bromo*iso*butyrate respectively (*cf.* Wilson and Burns, *J. Chem. Soc.*, 1922, **121**, 870; Chowdhury, Desai, Hunter and Solangi, *loc. cit.*), was, therefore, studied.



(I)

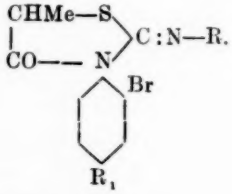


(II)

On treatment with bromine under the usual conditions, 2-phenylimino-3-phenyl-4-keto-5-methyltetrahydrothiazole (I, $R=R_1=R_2=H$) gave rise to an ill-defined hydroperbromide of a monobromosubstitution derivative, which on reduction with sulphurous acid yielded 2-phenylimino-3-*p*-bromophenyl-4-keto-5-methyltetrahydrothiazole (I, $R_2=R=H$; $R_1=Br$), whose constitution follows from its synthesis from *p*-bromo-*s*-diphenylthiocarbamide and ethyl α-bromopropionate (*cf.* Dains, Irvin and Harrel, *J. Amer. Chem. Soc.*, 1921, **43**, 613).

2-Phenylimino-3-phenyl-4-keto-5:5-dimethyltetrahydrothiazole (I, $R=R_1=H$; $R_2=Me$) showed, however, the closest resemblance to diphenyl-ψ-thiohydantoin (Farooq and Hunter, *loc. cit.*) and yielded a well defined vermilion hydropentabromide of 2-phenylimino-3-*p*-bromophenyl-4-keto-5:5-dimethyltetrahydrothiazole (II).

2-*p*-Tolylimino-3-*p*-tolyl-4-keto-5-methyltetrahydrothiazole (I, $R=R_1=Me$; $R_2=H$) resembled di-*p*-tolyl-ψ-thiohydantoin (Chowdhury, Desai, Hunter and Solangi, *loc. cit.*) in giving rise to a hydroperbromide which yielded 2-*p*-tolylimino-3-*o*-bromo-*p*-tolyl-4-keto-5-methyltetrahydrothiazole (III) ($R=C_7H_7$; $R_1=Me$) on reduction with sulphurous acid. The *gem*-dimethyl homologue ($I, R=R_1=R_2=Me$) behaved similarly on treatment with bromine, and gave rise to an idefinite hydroperbromide of 2-*p*-tolylimino-3-*o*-bromo-*p*-tolyl-4-keto-5:5-dimethyltetrahydrothiazole.



(III)

In contrast to 2-*p*-bromophenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole, however, 2-*p*-bromophenylimino-3-*p*-bromophenyl-4-keto-5-methyltetrahydrothiazole (I, $R=R_1=Br$; $R_2=H$) also underwent nuclear substitution by bromine in the 3-aryl substituent yielding a hydrotribromide of a tribromodiphenyl-ψ-thiohydantoin, whose constitution (III, $R=C_6H_4Br$; $R_1=Br$) was established by synthesis from *s*-*p*-bromophenyl-*o*-*p*-dibromophenylthiocarbamide and ethyl α-bromopropionate. The 5:5-dimethyl homologue (I, $R=R_1=Br$; $R_2=Me$) behaved similarly, and this difference in behaviour from

2-*p*-bromophenylimino-3-*p*-bromophenyl-4-ketotetrahydrothiazole may be attributed to the "electron source" properties of the methyl group and to the more sparing solubility of the tribromide of the latter ψ-thiohydantoin which is responsible for its early removal from the sphere of the reaction.

On the whole, the 5-methyl and 5:5-dimethyltetrahdrothiazoles, therefore, exhibit the closest similarity to the ψ-thiohydantoins studied in earlier investigations with regard to their behaviour towards bromine, in accordance with the original assumption that the keto-enol system in the latter plays no rôle in their bromination.

It has been suggested in earlier papers (Hunter, *J. Chem. Soc.*, 1930, 125; Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, **8**, 147; Farooq and Hunter, *loc. cit.*) that the labile bromine atoms in bromo-addition compounds of the type of benzthiazole dibromide are held to the nuclear nitrogen atom by means of singlet linkages. This suggestion was largely based on the existence of the hydrogen molecule ion $[H_2]^{\oplus}$ and the evidence of singlet linkages in pentahalides of the Fifth Group obtained from parachor measurements (Sugden, *J. Chem. Soc.*, 1927, 1176). It is now known, however, that the formation of molecules consists in the entry of electrons belonging to the atoms concerned into the *same group* of the electronic configuration of the molecule with resultant neutralisation of spin in accordance with Pauli's principle (Hund, *Z. Physik*, 1932, **73**, 1; **74**, 429). Teller's calculations (*Z. Physik*, 1930, **61**, 458) show moreover that a single electron does not possess bonding power, and that the formation of the hydrogen molecule ion depends essentially on the identity of the two positive hydrogen nuclei; this case has, therefore, nothing whatever to do with ordinary chemical linkage. In the production of the so-called singlet linkage, therefore, either the electron of the semipolar single bond forms a group with one or more electrons of the second atom, in which case it is an ordinary co-valency, or it is alone in a separate group and cannot constitute a real chemical linkage (Hunter and Samuel, *J. Chem. Soc.*, 1934, 1180).

With regard to the evidence of singlet linkages obtained from parachor measurements of pentahalides of the Fifth Group, Sugden (*loc. cit.*) assumes that the atomic parachor of phosphorus has a constant value of 37·7 and that the discrepancy between the observed parachor of phosphorus pentachloride and that calculated on the

assumption that the molecule contains five ordinary co-valencies arises from the presence of two singlet linkages. There is, however, the obvious alternative possibility that phosphorus possesses different parachor values in the trivalent and pentavalent states. This interpretation of Sugden's observations has been suggested by Sippel (*Ber.*, 1930, **63**, 2185) since it is well known that a reverse distribution of this type is conventionally assumed in molecular refractivity, which is very closely allied to the parachor. Indeed, the essential difference between the two constants is that whereas the direct relation between molecular refractivity and atomic constants follows from the Lorentz-Lorentz formula, which establishes the fact that this quantity is a measure of the polarisation to which a molecule is subject in the electromagnetic field of the light concerned, the basis of the parachor is an empirical formula the direct relation of which to atomic constants is still unknown. If phosphorus is assumed to possess different parachor values in the trivalent and pentavalent states and Sugden's value for chlorine is accepted, and the value for doubly bound oxygen is calculated from the empirical parachor of carbon dioxide, a value of $P^v = 18{\cdot}3$ may be deduced by subtraction from the observed parachor of phosphorus oxychloride (Sugden, Reed and Wilkins, *J. Chem. Soc.*, 1925, **127**, 1185). If this value is now used to calculate the parachor of phosphorus pentachloride, a value of 284·3 is obtained which approximates closely to the observed value of 282·5 (Sugden, *loc. cit.*)

It is, therefore, clear that parachor measurements cannot provide proof of the existence of singlet linkages in such compounds, and that some other explanation must be sought for the existence of the bromo-addition compounds of heterocyclic bases of the thiazole type. It is evident that there are at least two types of bromo-addition compounds formed between benzthiazole and bomine in inert solvents. The highly unstable complexes formed in many cases are probably mere dipole associations, but the exaraordinary stability of the dibromides of the 5-chloro-3-bromo-1-alkylaminobenzthiazoles (Dyson, Hunter, Jones and Styles, *loc. cit.*) suggests the presence of a pentavalent nuclear nitrogen atom, produced by the fission of the s^2 group of electrons (Hunter and Samuel, *loc. cit.*).

It is of course now clear that the hydrodibromides of the 1-amino-benzthiazoles cannot contain a $[Br_2^{\ominus}]$ ion involving a singlet linkage, and a specimen of 1-aminobenzthiazole hydrodibromide,

examined in Professor S. Bhatnagar's laboratory at Lahore, failed to exhibit the paramagnetism to be anticipated on the basis of an odd-electron structure. It is, therefore, probable that these hydrobromides are actually complexes of the type $[\text{Base, H}]_2\overset{\ominus}{\text{Br}}\ \text{Br}_2\ \overset{\ominus}{\text{Br}}$ (*cf.* Aliazam, Hunter and Noor Ahmad Khan, *J. Chem. Soc.*, 1934, 708).

Experimental.

2- *Phenylimino* -3- *phenyl* -4- *keto* -5- *methytetrahydrothiazole* (I) ($R=R_1=R_2=H$).—Ethyl α-bromopropionate (5·4 g.) was added to a solution obtained by treatment of thiocarbanilide (6·8 g.) in absolute alcohol (30 c.c.) with an equivalent of sodium ethoxide in absolute alcohol (20 c.c.), and the mixture was heated under reflux for 5·6 hours. The alcohol was removed on a water-bath and the residue was freed from sodium bromide by washing with water. On recrystallisation from alcohol it was obtained in small needles, m.p. 105°. (Found: S, 11·5. $C_{16}H_{14}ON_2S$ requires S, 11·3 per cent).

Bromination of (I, $R=R_1=R_2=H$).—A solution of the tetrahydrothiazole (1 g.) in chloroform (10 c c.) was treated with bromine (1 c.c. in 1 c.c. of the same solvent) at 0-3°, and the mixture was kept in ice for an hour. As no crystallisation took place the solution was concentrated under reduced pressure at laboratory temperature when a vermilion coloured bromo-addition compound separated, which was collected on porous earthenware and dried in a vacuum over potassium hydroxide, paraffin wax and anhydrous calcium chloride. An orange coloured microcrystalline *hydroperbromide* of a monobromo-substitution derivative of the tetrahydrothiazole was thus obtained which had m.p. 149° (decomp.). [Found: Br (total), 58·8; Br (labile), 27·9. $C_{16}H_{13}ON_2BrS$, $HBr(Br_2)$ requires Br (total), 53·2; Br (labile), 26·6 per cent]. On treatment with sulphurous acid and basification with ammonia this substance yielded 2-*phenylimino*-3-p-*bromophenyl*-4-*keto*-5-*methyltetrahydrothiazole*, which separated from alcohol in glistening needles, m.p. 121-122° (Found: Br, 22·3. $C_{16}H_{13}ON_2BrS$ requires Br, 22·2 per cent). It was also synthesised from ethyl α-bromopropionate and *p*-bromo-*s*-diphenylthiocarbamide thus.—A solution of *p*-bromo-*s*-diphenylthiocarbamide (1 g.) in absolute alcohol (10 c.c.) was treated with an equivalent of sodium ethoxide (in 5 c.c.

of absolute alcohol) and thereafter with ethyl α-bromopropionate (1 g.), and the mixture was heated under reflux for 5-6 hours. The methyltetrahydrothiazole obtained as in the previous case, separated from alcohol in needles, m.p. 122° (mixed m.p. 122°).

2-Phenylimino-3-phenyl-4-keto-5:5-dimethyltetrahydrothiazole (I) (R=R_1=H; R_2=Me).—A solution of thiocarbanilide (4·8 g.) in absolute alcohol (30 c.c.) was treated with an equivalent of sodium ethoxide (in 20 c.c. of the same solvent) and thereafter with ethyl α-*iso*bromobutyrate (3·9 g.), and the mixture was heated for 5-6 hours. It crystallised from alcohol in needles, m.p. 160°. (Found: S, 11·1. $C_{17}H_{16}ON_2S$ requires S, 10·8 per cent).

Bromination of (I, R=R_1=H; R_2=Me).—A solution of the dimethyltetrahydrothiazole (1 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of chloroform) at 0−3°, and the solution was kept in ice for 2 hours when a *hydropentabromide* separated in glistening vermilion plates, m.p. 196° (decomp. with effervescence, after softening at 130°) (after drying on porous earthenware in a vacuum) [Found: Br (total), 62·2; Br (labile), 41·2. $C_{17}H_{15}ON_2BrS$, $HBr(Br_4)$ requires Br (total), 61·8; Br(labile), 41·2 per cent]. This compound lost bromine on exposure to the atmosphere after 48 hours, yielding a yellow-orange product, having the composition of a hydrotetrabromide of the bromo-substitution derivative [Found: Br (labile), 34·5. $C_{17}H_{15}ON_2BrS$, $HBr(Br_3)$ requires Br (labile), 34·5 per cent]. On reduction with sulphurous acid, *2-phenylimino-3-p-bromophenyl-4-keto-5:5-dimethyltetrahydrothiazole* was obtained, which separated from alcohol in small needles, m.p 163°. (Found: Br, 21·1. $C_{17}H_{15}ON_2BrS$ requires Br, 21·3 per cent). It was also synthesised from ethyl α-bromo*iso*butyrate and *p*-bromo-*s*-diphenylthiocarbamide thus:—The dimethyltetrahydrothiazole prepared from *p*-bromo-*s*-diphenylthiocarbamide (1·5 g.) and ethyl α-bromo*iso*butyrate (1 g.), separated from alcohol in needles which had m.p. 163° (mixed m.p. 163°).

2-p-Tolylimino-3-p-tolyl-4-keto-5-methyltetrahydrothiazole, (I), (R=R_1=Me; R_2=H) prepared from *s*-di-*p*-tolylthiocarbamide (7·6 g.) and ethyl α-bromopropionate (5·4 g.) in the usual way, separated from alcohol in glistening needles, m.p. 110° (Found: S, 10·1. $C_{18}H_{18}ON_2S$ requires S, 10·3 per cent).

Bromination of (I, R=R_1=Me; R_2=H).—A solution of the methyltetrahydrothiazole in chloroform (1 g. in 10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of the same solvent) at 0−3°, and the solution was kept at this temperature for ½ hour and thereafter con-

centrated under reduced pressure at laboratory temperature. An indefinite orange bromo-addition compound was obtained, m.p. 92° (decomp., after softening at 69°). [Found: Br (labile), 23·5 per cent], which was reduced with sulphurous acid in the usual way. On basification with ammonia and recrystallisation from alcohol, 2-p-*tolylimino*-3-o-*bromo*-p-*tolyl*-4-*keto*-5-*methyltetrahydrothiazole* was obtained which formed glistening plates, m.p. 157°. (Found: Br, 20·7. $C_{18}H_{17}ON_2BrS$ requires Br, 20·5 per cent). It was also synthesised from *s*-*p*-tolyl-*o*-bromo-*p*-tolylthiocarbamide and ethyl α-bromopropionate. s-p-*Tolyl*-o-*bromo*-p-*tolylthiocarbamide*, prepared by condensation of *o*-bromo-*p*-tolylthiocarbimide (2·5 g.) and *p*-toluidine (2·1 g.) in methyl alcohol (15 c.c.), crystallised in small plates, m.p. 168°. The methyltetrahydrothiazole obtained from this thiocarbamide (1·7 g.) and ethyl α-bromopropionate (1 g.) in the usual way had m.p. 157° alone, and when mixed with the specimen already described.

2-p-*Tolylimino*-3-p-*tolyl*-4-*keto*-5:5-*dimethyltetrhydrothiazole* (I), (R=R_1=R_2=Me) prepared from *s*-di-*p*-tolylthiocarbamide (7·6 g.) and ethyl α-bromo*iso*butyrate (5·8 g.) in the presence of an equivalent of sodium ethoxide, separated from alcohol in small crystals, m.p. 167°. (Found: S, 10·1. $C_{19}H_{20}ON_2S$ requires S, 9·9 per cent).

Bromination of (I, R=R_1=R_2=Me).—An experiment similar to that already described in the case of 2-*p*-tolylimino-3-*p*-tolyl-4-keto-5-methyltetrahydrothiazole yielded an indefinite yellow-brown hydroperbromide, m.p. 98°. (after softening at 54°). [Found: Br (labile), 25·2 per cent], which was reduced with sulphurous acid in the usual way. On recrystallisation from dilute alcohol, 2-p-*tolylimino*-3-o-*bromo*-p-*tolyl*-4-*keto*-5:5-*dimethyltetrahydrothiazole* was obtained in cubes, m.p. 109° (Found: Br, 20·2. $C_{19}H_{19}ON_2BrS$ requires Br, 19·8 per cent). It was also synthesised from *s*-*p*-tolyl-*o*-bromo-*p*-tolylthiocarbamide and ethyl α-bromo*iso*butyrate. The tetrahydrothiazole obtained by condensation of *s*-*p*-tolyl-*o*-bromo-*p*-tolylthiocarbamide (1·7 g.) with ethyl α-bromo*iso*butyrate (1 g.), had m.p. 109° after recrystallisation, and was identical with the product obtained by bromination of 2-*p*-tolylimino-3-*p*-tolyl-4-keto-5:5-dimethyltetrahydrothiazole.

2-p-*Bromophenylimino*-3-p-*bromophenyl*-4-*keto*-5-*methyltetrahydrothiazole* (I) (R=R_1=Br; R_2=H) prepared from *s*-di-*p*-bromophenylthiocarbamide (10·6 g.) and ethyl α-bromopropionate (5·4 g.) in the usual way, had m.p. 120° after recrystallisation from alcohol (Found: Br, 36·6. $C_{16}H_{12}ON_2BrS$ requires Br, 36·4 per cent).

Bromination of (I, $R=R_1=Br$; $R_2=H$).—A solution of the tetrahydrothiazole (1 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of the same solvent) at 0—3°, and the solution was kept at this temperature for an hour and thereafter evaporated in a vacuum at laboratory temperature. A yellow *hydrotribromide* separated which had m.p. 86° (decomp. with effervescence, after softening at 74°). [Found: Br (total), 62·9; Br (labile), 23·0. $C_{16}H_{11}ON_2Br_3S$, HBr (Br_2) requires Br (total), 63·15; Br (labile), 21·05 per cent]. On reduction with sulphurous acid this bromo-addition compound yielded 2-p-*bromophenylimino*-3-o-p-*dibromophenyl*-4 *keto*-5-*methyltetrahydrothiazole*, which separated from alcohol in small crystals, m.p. 90°. (Found: Br, 46·4. $C_{16}H_{11}ON_2Br_3S$ requires Br, 46·2 per cent). It was also synthesised from *s*-*p*-bromophenyl-*o*-*p*-dibromophenylthiocarbamide. *s*-p-*Bromophenyl*-o-p-*dibromophenylthiocarbamide*, prepared by condensation of *o*-*p*-dibromophenylthiocarbimide (2·2 g.) with *p*-bromoaniline (1·3 g.) in benzene (20 c.c.), melted at 180°. (Found: Br, 51·9. $C_{13}H_9N_2Br_3S$ requires Br, 51·6 per cent). The gummy product obtained by condensation of this thiocarbamide with ethyl α-bromopropionate in the usual way, on recrystallisation from ethyl acetate yielded identical compound with that obtained in the bromination experiment already described.

2-p-*Bromophenylimino*-3-p-*bromophenyl*-4-*keto*-5:5-*dimethyltetrahydrothiazole* (I) ($R=R_1=Br$; $R_2=Me$), prepared by condensation of *s*-di-*p*-bromophenylthiocarbamide (7 g.) in absolute alcohol (60 c.c.) containing an equivalent of sodium ethoxide with ethyl α-bromo*iso*-butyrate (4 g.), separated from alcohol in fine needles, m.p. 165-66°. (Found: Br, 35·5. $C_{17}H_{14}ON_2Br_2S$ requires Br, 35·2 per cent).

Bromination of (I, $R=R_1=Br$; $R_2=Me$).—The *hydrotribromide* of 2-*p*-bromophenylimino-3-*o*-*p*-dibromophenyl-4-keto-5:5-dimethyltetrahydrothiazole obtained by bromination of the dimethyltetrahydrothiazole as in the case of the methyltetrahydrothiazole already described, formed a yellow microcrystalline powder, m.p. 84° (decomp., after softening at 50°). [Found: Br (total), 62·6; Br (labile), 19·4. $C_{17}H_{13}ON_2Br_3S$, HBr (Br_2) requires Br (total), 62·2; Br (labile), 20·7 per cent]. On reduction with sulphurous acid, this yielded 2-p-*bromophenylimino*-3-o-p-*dibromophenyl*-4-*keto*-5:5-*dimethyltetrahydrothiazole* which crystallised from dilute alcohol in needles, m.p. 140°. (Found: Br, 44·4. $C_{17}H_{13}ON_2Br_3S$ requires Br, 44·9 per cent). The identical compound, obtained from the tribromothiocarbanilide

(1 g.) and ethyl α-bromo*iso*butyrate, separated from dilute alcohol in needles which melted at 140° (mixed m.p. 140°).

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Halogenation. Part X. Preparation of Mixed Halogen Derivatives of Xylenes.

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The study of the literature shows that the chloro-iodo and bromo-iodo compounds of xylenes have not been obtained before. The majority of the mixed halogen derivatives of the aromatic hydrocarbons have usually been prepared by indirect methods from the diamino-compounds by successively replacing the amino groups by the halogen atoms by the Sandmeyer's reaction. Chlorotoluenes have been successfully iodinated in this laboratory in presence of sodium nitrite and fuming sulphuric acid or mixture of nitro-sulphonic and fuming nitric acids. (Varma and Sahay, *J. Indian Chem. Soc.*, 1934, **11**, 293).

It has been possible to iodinate the chloro- and bromoxylenes in presence of nitrosulphonic acid mixture and very good yields of the chloro-iodo and bromo-iodo compounds have been obtained. 2-Chloro-*p*-xylene and 4-chloro-*m*-xylene on iodination give two new chloro-iodo derivatives, which from analogy with the corresponding chloro and bromo derivatives seem to be 2-chloro-5-iodo-*p*-xylene and 4-chloro-6-iodo-*m*-xylene respectively. 4-Bromo-*o*-xylene on iodination and 4-iodo-*o*-xylene on bromination gave the same bromo-iodo derivatives of *o*-xylene. Hence the compound must be 4-bromo-5-iodo-*o*-xylene. In case of *m*-xylene, 4-bromo-*m*-xylene and 4-iodo-*m*-xylene, the former by iodination and the latter by bromination gave the same bromo-iodo-derivative. The compound in question is, therefore, 4-bromo 6-iodo-*m*-xylene. In the same way 2-bromo-*p*-xylene and 2-iodo-*p*-xylene gave the same bromo-iodo-*p*-xylene. The last compound seems to be 2-bromo-5-iodo-*p*-xylene from analogy with other halogen compounds of *p*-xylene.

6-Chloro 4-bromo-*m*-xylene has been prepared before (Noyes, *Amer. Chem. J.*, 1898, **20**, 798) from 6-bromo-4-amino-*m*-xylene. 2-Chloro-5-bromo-*m*-xylene has been obtained (Willgerodt and Wolfien, *J. pr. Chem.*, 1889, *ii*, **39**, 403) by the action of bromine on 2-chloro *p*-xylene. These compounds have been prepared by us in good yields by direct bromination in presence of nitro-sulphonic acid mixture and other substances.

Experimental.

2-*Chloro*-5-*iodo*-p-*xylene*.—To 2-chloro-*p*-xylene (5 c. c.), powdered iodine (5 g.), acetic acid (5 c. c.) and carbon tetrachloride (5 c. c.) in a flask with a reflux condenser, heated on a sand-bath the temperature of which was raised to about 135°, nitro-sulphonic acid mixture (4 c.c.) was added (1 c. c. at a time) in about 2 minutes. After the addition of the acid mixture the temperature of the sand-bath was raised to about 250° and maintained at that temperature for about 45 minutes. The reaction product was cooled, extracted with carbon tetrachloride, the extract being washed with a 5% solution of sodium hydroxide till free from iodine and then with distilled water, dried over fused calcium chloride and allowed to stand on a watch glass overnight, when crystals separated out. These were recrystallised from ether, m.p. 46°. (Found: total halogen, 60·05. C_8H_8ClI requires total halogen 60·98 per cent). It is easily soluble in carbon tetrachloride, chloroform, ether, benzene and xylenes. It is slightly soluble in methyl alcohol, cold acetic acid and more on warming, yield 7 g.

4-*Chloro*-6-*iodo*-m-*xylene*.—To 4-chloro-*m*-xylene (5 c. c.), powdered iodine (5 g.), acetic acid (5 c. c.) and carbon tetrachloride (5 c. c.) in a flask and heated on a sand-bath to about 145°, nitro-sulphonic acid mixture (4·5 c. c.) was added and then worked up as described before. The solid product (5·5 g.) was crystallised from warm acetic acid, m. p. 44°. (Found: total halogen, 60·15. C_8H_8ClI requires total halogen, 60·98 per cent).

4-*Bromo*-5-*iodo*-o-*xylene* (*i*) ***From* 4-*bromo*-o-*xylene*.**—To 4-bromo-*o*-xylene (5 c c.), powdered iodine (4·5 g.), acetic acid (5 c.c.) and carbon tetrachloride (4 c.c.) in a flask and heated on a sand-bath, nitro-sulphonic acid mixture (3 c.c.) was added drop by drop in about 15 minutes and the heating continued for about 2 hours more. The product was washed free of iodine by a dilute solution of caustic soda, dried over fused calcium chloride and left to stand overnight on a

watch glass when the temperature of the room was about 15°. Needle-shaped crystals separated out. Further crop of crystals was obtained from the mother liquor by cooling it in a freezing mixture, m. p. 68·5°, yield 4·2 g. (Found: total halogen, 66·03. C_8H_8BrI requires total halogen, 66·56 per cent). The solubility of the compound is the same as that of chloro-iodo derivatives.

(*ii*) *From* 4-*iodo*-o-*xylene*.—To 4-iodo-*o*-xylene (5 c.c.) and iodine (0·2 g.) in a flask with a reflux condenser, bromine (1·8 c.c.) was added drop by drop in about 10 minutes and the reaction product heated on a water-bath for about an hour more. The product was worked up as described above and the crystals isolated by cooling in a freezing mixture, m. p. 68·5°, yield 6 g. It is found to be identical with the compound obtained by iodinating 4-bromo-*o*-xylene. If bromination is conducted at the room temperature with aluminium chloride as a carrier the yield is 4·5 g.

4-*Bromo*-6-*iodo*-m-*xylene* (*i*) *From* 4-*bromo*-m-*xylene*.—To 4-bromo-*m*-xylene (5 c.c.), powdered iodine (5·5 g.), acetic acid (5 c.c.) and carbon tetrachloride (5 c.c.) in a flask, nitro-sulphonic acid mixture (3 c.c) was added drop by drop and heated for an hour more. The reaction product was worked up as described above. Needle shaped crystals (3·2 g.) were obtained, m. p. 47°. (Found: total halogen, 66·0. C_8H_8BrI requires total halogen, 66·56 per cent).

(*ii*) *From* 4-*iodo*-m-*xylene*.—To 4-iodo-*m*-xylene (3 c.c.) and iodine (0·1 g.) in a flask, bromine (2 c.c.) was added and the mixture heated on a water-bath for about 2 hours. The product was worked up as described above, yield 2·2 g. and with thallous chloride, 2·2 g.

2-*Bromo*-5-*iodo* p-*xylene* (*i*) *From* 2-*bromo*-p-*xylene*.—To 2-bromo-*p*-xylene (5 c.c.), iodine (4·5 g.), acetic acid (5 c.c.) and carbon tetrachloride (5 c.c.) in a flask and heated on a sand-bath to about 150°, nitro-sulphonic acid mixture (4 c.c.) was added (1 c.c. at a time) in about 15 minutes and then the temperature of the bath maintained at 230°-240° for about 45 minutes. The bromo-iodo compound was isolated by means of a freezing mixture as in the preceding cases. After crystallising from chloroform, the compound melted at 73°, yield 7·0 g. (Found: total halogen, 66·14. C_8H_8BrI requires, total halogen, 66·56 per cent).

(*ii*) *From*-2-*iodo*-p-*xylene*.—To 2-iodo-*p*-xylene (5 c.c.) and iodine (0·2 g.), bromine (1·8 c.c.) was added drop by drop in about 10 minutes and heated on a water-bath for about an hour. The bromo-iodo compound was isolated as before, yield 7·5 g. When the experiment

was conducted at the ordinary temperature without any halogen carrier, the yield was 4·3 g.

4-Chloro-6-bromo-m-*xylene*.—To 4-chloro-*m*-xylene (2 c. c.) and bromine (1 c.c.) in a flask and heated on a water bath, nitro-sulphonic acid mixture (1 c.c.) was added drop by drop and the heating continued for half an hour more. The product was worked up as described above. The crystals from ether melted at 68° and were identified to be 4-chloro-6-bromo-*m*-xylene, yield 3 g. In presence of sodium nitrite and fuming sulphuric acid the yield was 2·8 g. and in presence of iodine as carrier 2·6 g.

2-Chloro-5-bromo-p-*xylene*.—To 2-chloro-*p*-xylene (3 c.c.) and bromine (1 c. c.) in a flask, nitro-sulphonic acid mixture (1 c.c.) was added drop by drop and heated on a water bath for about 45 minutes. The chloro-bromo compound was obtained as described above and the crystals separated by cooling in a freezing mixture, m. p. 66°, yield 3·1 g. With strong nitric acid the yield was 2·8 g.

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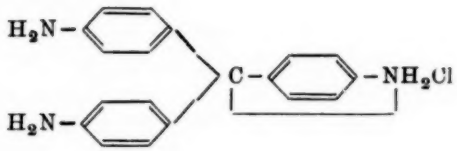
Parachor and Chemical Constitution. Part II. The Structure of the Triphenylmethane Dyes.

BY SUSIL KUMAR RAY.

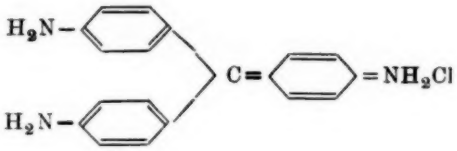
The constitution of the triphenylmethane dyes has been the subject of much controversy, the problem being not yet settled. The mother substances of the group, triphenylmethane and triphenyl carbinol are colourless. The *leuco*-bases as well as the dye-bases (when freshly prepared) are also colourless, while the salts are intensely coloured substances. It thus appears that there must be some fundamental difference in structure between the colourless and the coloured compounds. The colourless compounds are represented by benzenoid configuration while various formulæ have been proposed

from time to time by different investigators for the coloured salts of which the following are the most important:

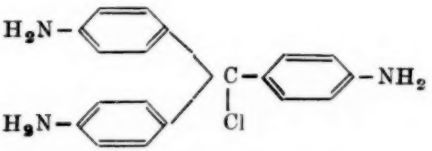
Rosaniline hydrochloride.



(Fischer, *Ber.*, 1878, **11**, 1079; 1879, **12**, 2351) $P_{calc}=724{\cdot}0$



(Nietzki, " Organische Farbstoffe," 1888.) $P_{calc}=741{\cdot}1$.



(Rosentiehl, *Bull. Soc. chim.*, 1880, **33**, 342, 426). $P_{calc}=717{\cdot}9$

The present work was undertaken with a view to find out which of the above formulæ agrees with the parachor contribution of the various triphenylmethane derivatives. The mother substance triphenyl carbinol, and the hydrochlorides of *para*-rosaniline (triaminotriphenyl carbinol), rosaniline (triaminodiphenyltolyl carbinol), crystal violet (hexamethyltriaminotriphenyl carbinol) and malachite green (tetramethyldiaminotriphenyl carbinol) have been studied. As the dye-bases cannot be kept colourless for a sufficiently long time in the air the coloured dye-bases of rosaniline and crystal violet, as well as the *leuco*-base of malachite green, have also been investigated.

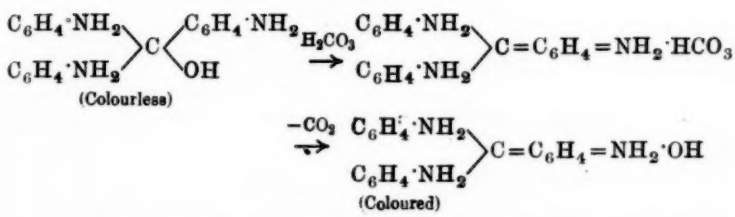
The surface tension was determined by the method of maximum bubble pressure as in the previous works. As the compounds decompose on fusion, it is not possible to determine their parachor in the fused state. The density and surface tension were determined in solution (Ray, *J. Indian Chem. Soc.*, 1934, **11**, 671) and the parachor calculated from the results obtained, P_x, was found to vary, except in a few cases, with x, the required parachor being obtained from the curve drawn by plotting P_x against x and finding the point of intersection with the ($x=0$) axis as in the previous work on carbohydrates (Ray, *ibid.*, 1934, **11**, 843). It will be found that with crystal violet colour-base and malachite green hydrochloride in pyridine, the value of P_x gradually increases with the increase of x, instead of decreasing. The required parachor can not be obtained in these cases from the curves as the point of intersection with the ($x=1$) axis can not be found, the points being too far from the ($x=1$) axis and too near the ($x=0$) axis, the solutions being extremely dilute.

It will be evident from the results given below that the parachor contributions of the coloured salts of the triphenylmethane agree with the quinonoid formula of Neitzki. Thus it appears that in solution these coloured salts possess the quinonoid configuration.

It is of much interest to note that the parachor values also suggest the quinonoid structure for the coloured dye-bases. In this connection it is to be noted that Georgievics (*Monatsh.*, 1896, **17**, 4) in the case of magenta, and Homolka in the case of ' New Fuchsin ' discovered a second rosaniline base which is coloured. The existence of this second rosaniline base was shown by Hantzsch and Ostwald (*Ber.*, 1900, **33**, 278) by electrical conductivity experiments.

Little work appears to have been done on the phenomenon of the change of colour of the dry carbinol-bases in presence of air. It was found that air is necessary for this colour change, as they can be kept colourless for a sufficiently long time in a vacuum desiccator. It was also found that this change is extremely rapid in the case of the carbinol base of crystal violet, while with the rosaniline base it is somewhat sluggish.

The author is of opinion that this change of colour is due to the migration of the OH group from the methane-carbon atom to a nitrogen atom of the amino group with the necessary transformation into the quinonoid configuration. It is difficult to explain the mechanism of this change; probably carbonic acid is instrumental in bringing about this transformation in the following way:



the carbonate being momentarily formed and then decomposed. This view is supported by the fact that colour appears rapidly when carbon dioxide is passed into the colourless solution while with oxygen the appearance of colour was not noted for a sufficiently long time. Moreover, the observations made by Georgievics (*loc. cit.*) that the solutions of coloured bases and the corresponding solution of the hydrochloride possess identical dyeing properties appear to suggest that the two have the same configuration. The structure suggested for the coloured bases by Georgievics (*loc. .cit*) is not in accordance with the results obtained by Weil (*Ber.*, 1896, **29**, 1541) and by the present author.

It will be seen that in the malachite green series, the variation of P_x is somewhat large. This is due probably to the presence of traces of impurities in these compounds as it is extremely difficult to purify them.

In the following tables x denotes the molar fraction of the solute, M_m, the mean molecular weight of the solution, P_m, the mean parachor and P_x, the parachor of the solute. The mean temperature of observation is about 28°. The results within parentheses are obtained from the curves given below.

TABLE I.

Triphenyl carbinol in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·0	0·9737	36·30	79·00	199·2	...	
0·006251	0·9754	36·36	80·11	201·7	607·8	611·9
0·007723	0·9769	36·56	80·39	202·3	608·5	
0·008515	0·9777	36·55	80·53	202·5	610·6	
0·001182	0·9796	36·68	81·15	203·8	583·7	
0·01523	0·9814	36·77	81·76	205·1	584·3	

TABLE II.

Triphenyl carbinol in chloroform.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·0	1·4640	25·97	119·37	184·1	...	
0·008151	1·4511	26·04	120·52	187·6	613·4	611·9
0·009795	1·4506	26·21	120·75	188·3	612·7	
0·01191	1·4502	26·34	121·09	189·2	612·5	
0·01530	1·4483	26·60	121·55	190·7	614·4	
0·02032	1·4398	26·57	122·18	192·7	611·0	

TABLE III.

Rosaniline hydrochloride in alcohol.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·7893	22·03	46	126·4	...
0·001353	0·7912	22·21	46·39	127·3	739·2
0·001625	0·7917	22·25	46·42	127·4	737·7
0·002018	0·7922	22·30	46·56	127·7	743·3
					mean 740·1

The calculated parachor for different formulæ has already been cited.

TABLE IV.

Rosaniline hydrochloride in alcohol.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·7893	22·03	46	126·4	...
0·001803	0·7900	22·06	46·53	127·6	776·7
0·002307	0·7910	22·10	46·68	127·9	780·3
0·003479	0·7935	22·35	47·01	128·7	776·2
0·005533	0·7965	22·40	47·62	130·0	777·3
					mean 777·6

The calculated parachor is as follows, parachor being shown in parenthesis: Quinonoid formula (780·1), Fischer's formula (763·0), Rosentiehl's formula (756·9).

TABLE V.

Rosaniline colour-base in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·9730	36·55	79	199·6	...
0·004279	0·9760	36·46	80·04	201·5	724·6
0·005034	0·9775	36·55	80·20	201·8	718·3
0·006036	0·9786	36·64	80·43	202·3	712·9
0·006823	0·9795	36·70	80·63	202·6	708·4
0·009170	0·9824	36·86	81·18	203·6	686·6
0·01397	0·9886	37·37	82·35	205·9	651·0
0·01416	0·9883	37·32	82·39	206·0	649·8
1·0	...	...	...	...	(758·0)

TABLE VI.

Rosaniline colour-base in quinoline.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	1·0941	44·67	130	307·2	...
0·005091	1·0943	44·80	130·85	309·5	766·1
0·006915	1·0942	44·96	131·11	310·3	762·4
0·007859	1·0944	44·90	131·30	310·7	763·5
0·009206	1·0952	45·16	131·51	311·3	760·3
0·01015	1·0952	45·17	131·70	311·8	758·8
0·01296	1·0960	45·34	132·25	313·0	757·7
					mean 761·5

The calculated parachor in parenthesis is as follows: Quinonoid formula (762·9), Fischer's formula (745·8), Rosentiehl's formula (739·7).

TABLE VII.

Crystal violet hydrochloride in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0 9737	36·30	79	199·2	...
0·003000	0·9760	36·48	79·98	201·4	933·3
0·003460	0·9765	36·51	80·15	201·8	924·7
0·005940	0·9785	36·50	80·93	203·8	892·3
0·007112	0·9805	36·56	81·35	204·0	871·8
0·008147	0·9816	36·63	81·59	204·5	859·2
1·0	...	...	...	...	(976·0)

TABLE VIII.

Crystal violet hydrochloride in chloroform.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	1·4640	25·97	119·37	184·1	...
0·002880	1·4609	26·17	120·27	186·2	935 4
0·004535	1·4592	26·24	120·75	187·4	926 0
0·005943	1·4563	26·31	121·12	188·3	891·9
0·007191	1·4557	26·38	121·43	189·0	876·0
0·01087	1·4549	26·52	122·53	191·0	818·5
1·0	..	...	...	...	(975·0)

The calculated parachor in parenthises is as follows:—Quinonoid formula (975·1), Fischer's formula (958·0), Rosentiehl's formula (951·9).

TABLE IX.

Crystal violet colour-base in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·9737	36·30	79	199·2	...
0·003546	0·9790	36·80	80·10	201·5	817·2
0·005720	0·9810	36·83	80·77	202·8	823·7
0·006723	0·9817	36·80	81·07	203·4	833·0
0·009122	0·9832	37·18	81·64	205·0	844·1

TABLE X.

Crystal violet colour-base in chloroform.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	1·4703	26·38	119·37	184·1	...
0·004488	1·4662	26·85	120·65	187·4	935·6
0·005610	1·4637	26·93	120·98	188·3	926·8
0·006725	1·4620	26·98	121·22	189·0	921·9
0·008110	1·4604	27·10	121·55	190·0	912·0
0·009387	1·4573	27·14	121·85	190·9	905·5
1·0	...	...	...	...	(957·1)

The calculated parachor in parenthesis is as follows:—Quinonoid formula (957·9), Fischer's formula (940·8), Rosentiehl's formula (934·7).

TABLE XI.

Malachite green leuco-*base in pyridine.*

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·0	0·9737	36·30	79	199·2	...	
0·603208	0·9799	36·77	79·75	201·3	841·6	837·1
0·005298	0·9809	37·53	80·09	202·6	830·7	
0·005613	0·9810	37·43	80·41	202·8	837·5	
0·005758	0·9812	37·46	80·44	202·9	833·4	
0·01246	0·9843	38·25	82·11	207·3	842·6	
					mean 837·2	

TABLE XII.

Malachite green hydrochloride in pyridine.

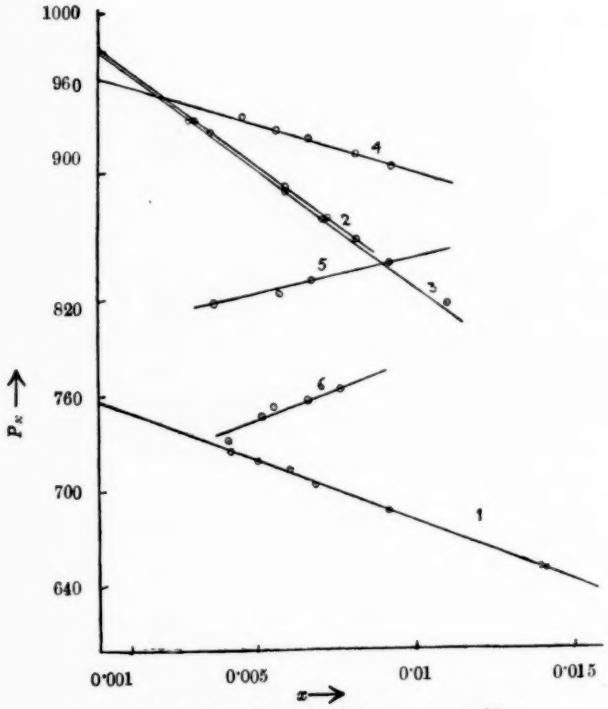
x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·9737	36·30	79	199·2	...
0·004112	0·9770	36·34	80·16	201·4	729·7
0·005226	0·9783	36·36	80·47	202·1	746·3
0·005448	0·9806	36·81	80·56	202·3	752·6
0·006615	0·9816	36·81	80·88	202·9	756·0
0·007608	0·9820	36·67	81·16	203·5	762·3

TABLE XIII.

Malachite green hydrochloride in nitrobenzene.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	1·1997	42·36	123	261·4	...
0·003858	1·2010	43·06	124·01	263·8	907·8
0·004416	1·1996	42·66	124·11	264·2	905·9
0·006258	1·2020	43·01	124·48	265·3	894·8
0·006628	1·2022	43·09	124·62	265·5	890·2
0·007008	1·2034	43·20	124·76	265·8	899·1
					mean 899·6

The calculated parachor in parenthesis is as follows:—Quinonoid formula (897·5), Fischer's formula, (880·4), Rosentiehl's formula, (874·3).



1. Rosaniline colour-base in pyridine
2. Crystal violet hydrochloride ,,
3. Do Do in $CHCl_3$
4. Do colour-base ,,
5. Do Do in pyridine
6. Malachite green hydrochloride ,,

SUMMARY.

1. The surface tension and density of the hydrochlorides and coloured carbinol-bases of rosaniline, crystal violet and malachite green have been determined in solution and the parachor calculated.

2. The parachor values were found to agree with the quinonoid structure suggested by Nietzki.

My grateful thanks are due to Prof. P. R. Rây of the University College of Science and to Prof. A. Maitra of the Presidency College for the kind interest they took in the work.

CHEMICAL LABORATORY,
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Received December 14, 1934.

A Yellow Colouring Matter from the Wood of *Adina Cordifollia*, Hook.

BY JAGARAJ BEHARI LAL AND SIKHIBHUSHAN DUTT.

Adina cordifolia (Hook) which is known as "Keli-Kadam" in Bengal and "Naldu" in Hindusthani, is a large deciduous tree which is found to be fairly well distributed throughout the whole of northern India as well as Bengal, Assam and Burma. In most of the forests it grows profusely and very often it is planted as a road-side or avenue tree. The wood is very even-grained, moderately hard, lemon-yellow in colour when freshly cut but turning yellowish grey on exposure and weighs 45 pounds per cubic foot. It is suitable for furniture making and in northern India combs are made out of this wood as well as toys and drums. The colouring matter of this wood is very easily removed by extraction with boiling water or organic solvents and as no work seems to have been done before on this subject, the present investigation was undertaken with a view to the isolation of the colouring matter in a pure state and elucidation of its constitution.

EXPERIMENTAL.

A big log of the authentic specimen of the wood was procured from Messrs. Bhupat Lal & Sons, Wood Merchants, Allahabad, and was converted into shavings. For exhaustive extraction with

different solvents, the coarsely powdered shavings were taken in 20 g. lots in a Soxhlet's extractor, and after filtration, the solvent was evaporated in each case and the residue brought to a constant weight by heating in a steam-oven. The following results were obtained.

Aqueous extract.—The extract was bright yellow at first, but during the course of heating in the steam-oven, it gradually became brown. Microscopic examination revealed the presence of colourless crystals of calcium oxalate and the substance gave strong reactions of tannins and sugars, yield 5·18%. No essential or fixed oil could be detected.

Chloroform extract.—The substance was a pale yellow wax, yield 0·02%.

Petroleum ether extract.—This was practically identical with the chloroform extract, yield 0·03%.

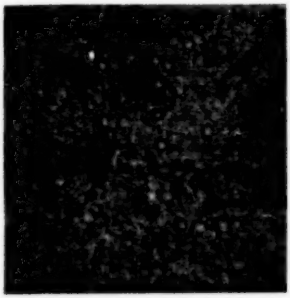
Acetone extract.—It was a light yellow semi-solid substance with colourless crystals of calcium oxalate disseminated throughout the entire mass, yield 3·67%. In general properties it is quite similar to the alcoholic extract.

Alcoholic extract.—It was an orange-yellow semi-solid mass with a characteristic smell of the wood and a slight astringent taste, yield 6·88%. It gives a green colouration with neutral alcoholic ferric chloride, a pale yellow precipitate with alcoholic lead acetate and an intense yellow colouration with concentrated sulphuric acid. Caustic alkalis yield a yellowish brown colouration which darkens on exposure to the air. The substance reduces Fehling's solution and ammoniacal silver nitrate and gives negative tests with alkaloid reagents. Calcium oxalate is present in the substance in fairly large quantities and can be easily isolated.

Isolation of Adinin.

1 Kg. of small shavings of the wood was repeatedly extracted with 95% alcohol in a 5 litre extraction flask until the extract was practically colourless. The combined orange-yellow extracts were distilled at the ordinary pressure until practically the whole of solvent had distilled over and the residue began to froth vigorously. It was then allowed to stand for a week at the end of which a large amount of crystalline matter separated out in the form of yellow nodules. This was filtered off, washed with small quantities of alcohol and dried in the steam-oven. The substance was then freed from waxy impurities by extraction with hot benzene and the

purified material thus obtained was recrystallised several times from hot alcohol. The pure substance crystallises from alcohol in long,



Adinin from acetic acid (× 250)

Adinin from alcohol (× 250)

fine, glistening needles with a golden yellow colour and from glacial acetic acid in small bright yellow prisms the microphotographs of which are shown above. The substance on heating darkens in colour at 195°-96° becoming orange-red, shrinks at 200° and above that temperature gradually darkens and decomposes without melting. The substance is practically insoluble in cold and only slightly soluble in boiling water and undergoes decomposition on protracted boiling. It is insoluble in chloroform, carbon tetrachloride, benzene, ether, petroleum ether and carbon disulphide. It is slightly soluble in cold and moderately soluble in hot alcohol, acetone and glacial acetic acid. It dissolves readily in solutions of alkali hydroxides but less readily in alkali carbonates and bicarbonates, forming light yellow solutions, from which the colouring matter is reprecipitated unchanged on acidification. The substance although neutral in reaction, dissolves in concentrated mineral acids like hydrochloric, hydrobromic, hydroiodic, nitric and sulphuric acids, forming bright yellow solutions, the colours of which are much more intense than that of the corresponding concentration of the colouring matter in alcoholic solution. Alcoholic solution of the substance gives no precipitate or colouration with alcoholic ferric chloride, lead acetate, calcium chloride or silver nitrate. The substance does not reduce Fehling's solution either before or after boiling with concentrated hydrochloric acid, thereby showing its non-glucosidal nature. The substance in alcoholic hydrochloric acid on treatment with metallic

magnesium becomes reduced to a colourless substance thereby showing that it is not a colouring matter belonging to the flavone groups which by this treatment would have been reduced to a red or violet coloured flavylium salt. The alcoholic solution of the substance shows a bright green fluorescence which becomes more intense in ultraviolet light, in which also the substance dissolved in concentrated sulphuric acid shows a violet flourescence and its solution in phenol a greenish blue fluorescence. These apparently point to the presence of an anthraquinone, a xanthone or an *iso*flavone nucleus in the molecule. The absence of an anthraquinone nucleus was proved by the fact that on treatment with zinc dust and ammonia it did not give any red, blue or violet colouration, but became altogether colourless.

In alcoholic solution it is optically inactive. From 10 kg. of the shavings 9·1 g. of the pure substance were isolated (yield 0·09%). [Found (specimen dried at 120°): C, 60·58, 60·28, 60·50, 60·32; H, 4·63, 4·83, 4·51, 4·64. M. W. (cryoscopically in phenol), 299, 293, 290. $C_{16}H_{14}O_7$ requires C, 60·4; H, 4·4 per cent. M.W., 318]. [Found (specimen dried in vacuum desiccator for 10 days): C, 56·55, 56·83; H, 4·83, 4·85. $C_{16}H_{14}O_7$, H_2O, requires C, 57·1 ; H, 4·8 per cent]. The air-dried substance lost 16·2, 15·9, 16·3% of H_2O at 120° and 9·8, 9·6% of H_2O in the vacuum desiccator in the course of 10 days. $C_{16}H_{14}O_7$, $3H_2O$ requires for loss of $2H_2O$, 9·67% and for loss of $3H_2O$, 14·7%.

It is clear from the analytical data that the substance crystallises from 95% alcohol with three molecules of water of crystallisation of which it loses two in the vacuum desiccator and all the three at 120°. No compound of this formula and possessing properties identical with it has been recorded in chemical literature. It is therefore, proposed to designate this new compound "adinin" with reference to its properties as a colouring matter and the generic name of the plant from which it has been isolated.

Demethylation of adinin.—A carefully weighed amount of adinin dried at 120° was heated with freshly distilled hydroiodic acid (*d*, 1·72) in accordance with the method of Zeisel for the estimation of methoxy groups. The precipitated silver iodide was filtered off, washed with dilute nitric acid, dried at 120° and weighed. (Found: OMe, 10·1, 9·9. $C_{15}H_{11}O_6 \cdot OMe$ requires OMe, 9·74 per cent).

nor*Adinin*.—The collective product from the action of hydroiodic acid, which was evidently present in the form of an oxonium salt, was

poured into sodium hydrogen sulphite solution, and the yellow precipitate collected. It crystallises from boiling glacial acetic acid in the form of yellow needles which shrink at 213-14° and decomposes above 232° without melting. It is practically insoluble in cold or hot water, alcohol, acetone, benzene, ether, chloroform and petroleum ether and is fairly soluble in hot acetic acid. Alcoholic ferric chloride gives a dirty greenish grey colour with the alcoholic solution of the substance and alcoholic lead acetate throws down a pale yellow precipitate. *nor*Adinin has not yet been obtained in sufficient quantity for combustion.

Adinin hydrobromide.—Adinin (0·5 g.) dried at 120° was treated with the minimum quantity of concentrated hydrobromic acid (*d* 1·78), sufficient to dissolve it. The substance dissolved immediately forming an intense yellow solution and the clock-glass containing it was kept in a vacuum desiccator containing granulated solid caustic potash for a number of days. The product when completely dry was washed with dry ether and finally dried in the vacuum desiccator. The hydrobromide was thus obtained in the form of bright orange-yellow needles which shrink at 159-60° and decompose above 200° without melting. (Found: Br, 22·6. $C_{16}H_{14}O_7$, HBr requires Br, 20·05 per cent).

Ammonium salt of adinin was obtained by dissolving 0·5 g. of adinin in the smallest quantity of pure concentrated ammonia and allowing the solution to evaporate at the ordinary temparature in a desiccator over concentrated sulphuric acid for several days. The salt was obtained as orange-yellow crusts which shrink at 104°-5°, completely melt at 130°, solidify and again melt at 202°-3° with frothing. On exposure to air it gradually loses ammonium and becomes converted into a mixure of adinin and the ammonia salt of varying composition. The substance could not be obtained in a state of sufficient purity for analysis.

Absorption spectra of adinin.—An alcoholic solution of adinin (1%) on spectrographic examination was found to have a well-defined absorption band between wave-length 4250-4650Å, with the head of the band or absorption maxima at 4590Å.

One of us (J. B. L.) wishes to express his indebtedness to the Kanta Prasad Research Trust of the Allahabad University for a scholarship which enabled him to undertake this investigation.

Received January 11, 1935.

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Chemical Examination of *Butea Frondosa* Flower. Isolation of a Crystalline Glucoside of Butin.

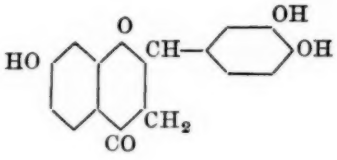
By Jagaraj Behari Lal and Sikhibhushan Dutt.

Butea Frondosa, called *Dhak* or *Palas* in Hindusthani is a fine tree belonging to the natural order of *Leguminoseæ* and is very common in India. The flowers, which in the dried state are known as *tisu* or *palas-ke-phul*, have either a bright yellow colour with bright orange spots or have an orange colour with red spots. They are the source of one of the few surviving members of a large number of natural organic colouring matters and are still used in India especially in the United Provinces. Large quantities of the flowers are collected in March and April and employed by the people to produce a yellow dye much used during the "Holi Festival." "The flowers are supposed to be astringent, depurative, diuretic and aphrodisiac; as a poultice they are much used to disperse swelling and promote diuresis and the menstrual flow. They are given to enciente women in the case of diarrhœa, and are applied externally in orchitis" Kirtikar and Basu, "Indian Medicinal Plants", 1918, Part I, p. 443).

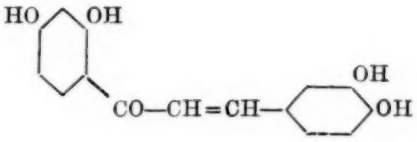
A preliminary examination of these flowers was made by Hummel and Caralls (*Proc. Chem. Soc.*, 1894, **10**, 11) who isolated a substance termed "butein" $C_{15}H_{14}O_5$, and supposed this to be the true colouring matter. This product in some respects yielded shades which were not unlike those of fisetin obtained from young fustic. Hill (*Proc. Chem. Soc.*, 1903, **19**, 133) extracted from these flowers a colouring matter in the form of lemon-yellow crystals which gave the reactions of fisetin. He noted further the presence of a phlobaphene which on fusion with caustic potash gave phloroglucinol and protocatechuic acid. Finally Hummel and Perkin (*Proc. Chem. Soc.*, 1903, 134; *J. Chem. Soc.*, 1904, **85**, 1463) examined the flowers and isolated by acid hydrolysis of the aqueous extract a colourless crystalline compound, butin $C_{15}H_{12}O_5$ melting at 224-26° and traces of an orange-red crystalline substance, butein $C_{15}H_{12}O_5$ melting at 213-15° in 0·04% yield. They also proved the non-occurrence of fisetin in the flowers and were of opinion that they

contain but a trace of free butin or butein. As a result of the dyeing tests with mordanted calico, they assumed that butin and butein were present in the form of glucosides which they failed to isolate.

The constitutions which Perkin and Hummel (*loc. cit.*) assigned to butin and butein are those of 7:3′:4′-trihydroxyflavanone (I) and 2:4:3′:4′-tetrahydroxychalkone (II) respectively and they established the correctness of these formulæ by the synthesis of butin and butein trimethyl ether.



(I)



(II)

Somewhat later Göschker and Tambor (*Ber.*, 1911, **44**, 3502) prepared butein itself by treating protocatechuic aldehyde and resacetophenone in boiling alcohol with potassim hydroxide and found it to be identical in all respects with the natural product. Later on attempts of Shinoda, Sato and Kawagoe (*J. Pharm. Soc. Japan*, 1929, **49**, 123) to repeat their synthesis were unsuccessful. They, however, succeeded in synthesising butein by the condensation of the acid chloride of dicarbethoxycaffeic acid with resorcinol.

In view of the uncertainty as to the probable existence of a glucoside in the flowers the present authors undertook a critical investigation and have isolated a colourless crystalline glusoside, $C_{27}H_{32}O_{15}$, $2H_2O$ melting sharply at 193·5° and giving on hydrolysis two molecules of glucose and one of butin. A satisfactory process for the isolation of the diglucoside of butin, the first recognised member of the flavanone group, has been worked out. The glucoside has

been termed butrin in view of the fact that it is a glucoside of butin. The yield of butrin is on the whole 2·6% and that of the phlobaphene and of butein isolated are 1% and 0·003% respectively.

Experimental.

Dried flowers were obtained from the local market and their petals were collected and ground to a coarse powder. The powdered flower-petals were extracted in 50 g. lots in a Soxhlet's apparatus with various organic solvents. The solvent was subsequently evaporated and the extract thus obtained dried to a constant weight at 100°. The results are given below.

Alcoholic extract.—Orange-yellow, soft crystalline mass with a peculiar odour. It gives an olive-green colour with ferric chloride, a brownish-yellow granular precipitate with lead acetate and reduces Fehling's solution. Microscopic examination of the substance revealed the presence of an yellow crystalline colouring matter, a colourless crystalline substance, a wax and chlorophyll, yield 21·46%.

Acetone extract.—Similar to the alcoholic extract, but much lighter in colour. A lemon-yellow crystalline substance could be easily discerned through the matrix of sticky matter, yield 13·56%.

Ethyl acetate extract.—Light yellow semi-solid substance containing crystalline matter in suspension, yield 5·5%. It had properties similar to the above.

Benzene extract.—Light yellow substance with properties similar to the above, yield 0·01%.

The dried flowers when completely incinerated left 11·52% of flesh coloured ash containing 2·98% of water-soluble and 8·54% of water-insoluble inorganic constituents. The water-soluble portion was mainly potassium carbonate with traces of sodium phosphate and chloride. The water-insoluble portion contained calcium, magnesium aluminum and traces of zinc together with sulphate, phosphate and carbonate.

Isolation of butrin.—For complete examination, 4 kg. of the coarsely powdered flowers were in lots of 700 g. repeatedly extracted with rectified spirit in a 5 litre extraction flask until the extract was no longer coloured. The combined orange-yellow extracts were distilled until most of the solvent had been recovered and the residue boiled with frothing. It was then allowed to stand at the ordinary temperature for about a week by which time a large amount of soft crystalline matter had separated out. The thick crystalline magma

was slightly thinned by the addition of about one tenth of its volume of alcohol and filtered at the pump with good suction. The residue was washed with alcohol, until it had assumed a lemon-yellow colour. After drying at first in the air and then in the steam-oven it was obtained as an yellow crystalline gritty mass melting at 135-39° and it was of a glucosidal nature. It was repeatedly extracted with hot benzene in order to remove chlorophyll and waxy matter. Then it dissolved fairly readily in cold water and this rather unusual property suggested that it was probably a salt of the dyestuff and on examination it proved to be the case since it contained potassism in organic combination in considerable quantity. By repeated crystallisations from alcohol it could only be obtained as a soft yellow crystalline mass containing, in between, clusters of white tiny needles. The substance on repeated extraction with boiling acetone gave a very small amount of an intensely sweet substance which was not further examined. The melting point of the substance rose to 190° after three crystallisations from hot water when it was obtained in the form of tiny colourless needles and after two crystallisations from alcohol the melting point rose to 193·5° and did not rise any further. This substance on slow and careful crystallisation is obtained in the form of glistening needles often as long as 1 cm. The dried substance has the composition $C_{27}H_{32}O_{15}$, $2H_2O$ and loses the two molecules of water of crystallisation when heated at 120° for 15 hours. The anhydrous substance is extremely hygroscopic and readily absorbs two molecules of water of crystallisation when exposed to air. It has all the properties of a glucoside since it reduces Fehling's solution only after hydrolysis with mineral acids. Further crops of the lemon-yellow gritty mass were obtained by concentrating the successive mother-liquors and the aqueous washings but they required, after removal of waxy matter and chlorophyll, several crystallisations from hot water before they were sufficiently pure to be crystallised finally from alcohol.

It is slightly soluble in cold water to a perfectly colourless solution which remains undecomposed on boiling. It is insoluble in acetone, ether, benzene, bromoform, carbon tetrachloride, chloroform and petroleum ether; slightly soluble in cold and moderately soluble in hot ethyl and methyl alcohols and glacial acetic acid and is very readily soluble in pyridine to a colourless solution. In caustic alkalis and alkali carbonates, however, it dissolves to a deep yellow solution and on boiling it undergoes decomposition giving a deep orange solution. It gives no precipitate in alcoholic solution with silver

nitrate and calcium chloride, but gives a pale yellow precipitate with lead acetate. It does not give any colouration with alcoholic ferric chloride; with excess of methyl or ethyl alcoholic hydrochloric acid and magnesium powder it gives an intense violet colouration which turns brown on dilution with water, thereby showing that the substance is a flavanone derivative (Tsujimura, *Bull. Inst. Phys. Chem. Res. Tokyo*, Vol. VI, 12, III; Kuroda, *J. Chem. Soc.*, 1930, **137**, 753). It gives an intense red colouration with concentrated hydrochloric acid which disappears on dilution. With concentrated sulphuric acid it first turns orange-red and finally dissolves to an orange-red solution which turns deep red on warming. It does not contain any OMe or OEt groups. [Found: loss of H_2O at 120°, 5·84, 5·79; $C_{27}H_{32}O_{15}$, $2H_2O$ requires H_2O, 5·69%. The air-dried substance gave on combustion C, 51·24, 51·26, 51·21; H, 5·69, 5·84, 5·78; and the fully dried substance gave C, 54·32, 54·19; H, 5·67, 5·64. $C_{27}H_{32}O_{15}$, $2H_2O$ requires C, 51·26; H, 5·69%; and $C_{27}H_{32}O_{15}$ requires C, 54·3; H, 5·6 per cent].

Isolation of butein.—A portion of the filtrate after the separation of the butrin was treated with excess of hot alcoholic lead acetate and the resulting bright orange-yellow precipitate filtered off and washed first with alcohol and then with hot water. This on decomposition with hydrogen sulphide in alcoholic suspension and after filtering off the lead sulphide gave a deep orange solution which on concentration deposited no crystalline mass. It was treated with hot water when a viscous deep red mass separated and the latter on repeated extraction with water left behind a phlobaphene melting at 115° which was also isolated by Hill (*loc. cit.*).

The aqueous solutions after concentration at first under ordinary pressure and then under reduced pressure slowly deposited a small amount of an orange precipitate, which on repeated crystallisations from dilute alcohol was obtained in the form of bright yellow needles melting at 213-15°. It gave an olive-brown colouration with alcoholic ferric chloride, a deep red precipitate with alcoholic lead acetate and dissolved in alkalis and alkali carbonates to a deep orange-red solution. It was identified to be butein which Perkin (*loc. cit.*) isolated in traces from the flowers of *Butea Frondosa*. [Found (dried at 160°): C, 66·07; H, 4·57. $C_{15}H_{12}O_5$ requires C, 66·17; H, 4·41 per cent].

The alcoholic filtrate and washing from the lead acetate precipitate gave a bright yellow precipitate on treatment with excess

of basic lead acetate. This on working up in accordance with the method described above gave an orange-yellow solution which on concentration deposited a considerable quantity of an yellow crystalline mass which on purification was found to be butrin. No other glucoside or substance of interest could be isolated from these mother-liquors.

Hydrolysis of Butrin and Formation of Butin.

Butrin (2 g.) was hydrolysed by heating with dilute sulphuric acid (5%, 100 c.c.) under reflux on the water-bath for 2 hours. The substance gradually dissolved forming a light yellow solution, which on standing for several days deposited a quantity (0·8 g.) of pale yellow needles. These on several recrystallisations from alcohol were obtained as a practically colourless substance crystallising in needles and melting at 224-25° identified as the butrin of Perkin. [Found (in the substance dried at 140°): C, 66·07; H, 4·41. $C_{15}H_{12}O_5$ requires C, 66·27; H, 4·4 per cent].

The mother liquor, left after the hydrolysis of butrin, reduced Fehling's solution strongly and on treatment with phenylhydrazine gave an osazone which melted at 202° and was identical with phenylglucosazone. The sugar contained in butrin, therefore, must be glucose, and the former must be the di-glucoside of butin.

One of us (J. B. L.) wishes to express his indebtedness to the Kanta Prasad Research Trust of the Allahabad University for a scholarship which enabled him to take part in this investigation.

Further work on this subject is in progress.

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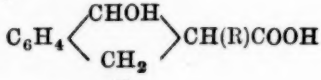
The Rates of Racemisation of Acids of the Type $R_1(R_2)CH{\cdot}COOH$.

By B. K. Menon and D. H. Peacock.

Acids of the type $R_1R_2CH{\cdot}COOH$ are readily racemised if R_1 and R_2 are aromatic groups but are racemised only with difficulty if one of the groups is aliphatic. Thus Kipping and Hunter (*J. Chem. Soc.*, 1903, **83**, 1009) showed that α-methyl-β-phenylpropionic acid was not at all readily racemised, while Rupe and Kerkovins (*Ber.*, 1912, **45**, 1398) found that αβ-diphenylpropionic acid was readily racemised and similar behaviour was observed by McKenzie and Widdows (*J. Chem. Soc.*, 1915, **107**, 702) in the case of phenyl-*p*-tolylacetic acid. We have prepared and examined acids of the type (I).



(I)

These acids readily undergo inversion at the α-carbon atom when R is $PhCH_2-$, $p\text{-}BrC_6H_4CH_2-$, or $PhCH_2CH_2-$, but not when R is Me or *n*-Bu (Peacock and Menon, *J. Chem. Soc.*, 1934, 1296; 1935, 15). In the present paper the behaviour of acids of the type, R R′CH·COOH (II) is described.

The acids examined are:

(1) α-Benzyl-*n*-caproic (II, R = *n*-Bu ; R′ = $PhCH_2$)
(2) α-*p*-Bromobenzyl-*n*-caproic (II, R = *n*-Bu ; R′ = $p\text{-}BrC_6H_4CH_2$)
(3) α-Benzyl-β-*p*-bromophenylpropionic (II, R = $PhCH_2$; R′ = $p\text{-}BrC_6H_4CH_2$)
(4) α-Benzyl-β-*m*-bromophenylpropionic (II, R = $PhCH_2$; R′ = $m\text{-}BrC_6H_4CH_2$)
(5) α-Benzyl-β-*p*-chlorophenylpropionic (II, R = $PhCH_2$; R′ = $p\text{-}ClC_6H_4CH_2$)
(6) α-Benzyl-β-*m*-chlorophenylpropionic (II, R = $PhCH_2$; R′ = $m\text{-}ClC_6H_4CH_2$).

No systematic examination of acids of this type appears to have been made and the object of the present work was to

confirm the accelerative effect of aromatic groups and to search for an alternating effect by substituents in the aromatic nucleus. In the following table are given the times of half racemisation for these acids.

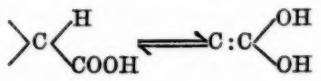
TABLE I.

Racemisation velocities.

Acid.	Half racemisation time.
α-Benzyl-*n*-caproic	18 hr. (approx.)
α-*p*-Bromobenzyl-*n*-caproic	18 (approx.)
α-Benzyl-β-*p*-bromophenylpropionic	1·5
α- ,, *m*- ,, ,,	1·0
α- ,, *p*-Chlorophenylpropionic	1·5
α- ,, *m*- ,, ,,	1·9

It will be seen that replacement of the *n*-butyl group by the benzyl or *p*-bromobenzyl group greatly increases the rate of racemisation. The first two acids were racemised so slowly that the rates are not accurate enough to decide whether the introduction of the bromine atom exerts any influence. Certainly any effect cannot be great. When the *para*-substituted acids are compared it is seen that chlorine and bromine exert similar effects but that with the halogen in the *meta*-position the bromo-acid racemises faster than the chloro-acids. Comparing the effect of each halogen in the *p*- and *m*-positions it is seen that with chlorine the *p*-acid reacts faster than the *m*-, while with bromine the *p*- acid reacts more slowly than the *m*-.

Kipping and Hunter (*loc. cit.*) suggested that the racemisation of α-substituted acids was due to enolisation:—



Gadamer (*J. pr. Chem.*, 1913, *ii*, **87**, 312), who found that the ethyl ester of tropic acid was racemised more readily than the sodium salt, suggested that the α-hydrogen atom was ionised:—

$$PhCH(CH_2OH)CO_2Et \rightleftharpoons Ph\overset{\ominus}{C}(CH_2OH)CO_2Et + \overset{\oplus}{H}$$

and the ionised molecule then underwent racemisation. He pointed out that there was a causal relationship between the ionisability of

one of the groups attached to the asymmetric carbon atom and racemisation and that the α-H atom was able to be ionised owing to the negative character of the groups attached to the α-carbon atom. This explanation has been extended by Ingold and Wilson (*J. Chem. Soc.*, 1934, 773) who found that the rate of racemisation of 2-*o*-carboxybenzylindan-1-one was very nearly equal to its rate of bromination. As the rate of the latter reaction is generally regarded as determined by the rate of expulsion of a proton, the approximate equality of the two rates of reaction supports the suggestion that both are determined by the ease of proton expulsion. Racemisation is thus a special case of proton tautomerism and is favoured by the entry of electron attracting groups (*cf.* Wilson, *J. Chem. Soc.*, 1934, 98). The results described in this paper support this view; replacement of the butyl group by the more strongly electron attracting groups, benzyl or *p*-bromobenzyl, accelerates the rate of racemisation.

The halogenated acids can be considered from two points of view, firstly as affording data for a comparison of the effect of replacing chlorine by bromine and secondly as giving information as to the working and existence of an alternating effect. Replacement of of bromine by chlorine in benzene derivatives does not always produce consistent results. *p*-Chloroaniline reacts faster than *p*-bromoaniline with both benzyl bromide and 2:4-dinitrochlorobenzene (Peacock; Peacock and Attar Singh, unpublished data). Davies and Lewis (*J. Chem. Soc.*, 1934, 1601) observed similar effects with the substituted dimethylanilines. The reactivity of an amine is usually regarded as being increased by increased electron availability at the nitrogen atom so that in these cases the replacement of bromine by chlorine apparently increases electron availability at the *para*-position in the benzene ring. This conclusion is confirmed by the results obtained by Flürscheim (*J. Chem. Soc.*, 1910, **97**, 84) who showed that *p*-chloroaniline was a stronger base than *p*-bromoaniline. On the other hand Kuhn and Wassermann (*Helv. Chim. Acta*, 1928, **11**, 31) showed that *p*-chlorobenzoic acid was a slightly stronger acid than *p*-bromobenzoic acid thus indicating that electron availability in the *p*-carboxyl group was less in the chloro-acid than the bromo as ionisation is favoured by electron attracting groups. Olivier (*Rec. trav. chim.*, 1922, **41**, 646; 1930, **49**, 697) showed that *p*-chlorobenzyl chloride was hydrolysed more rapidly than *p*-bromobenzyl bromide; in this reaction electron accession to the carbon atom of the CH_2Cl group is

regarded as favouring reactivity so that here the replacement of bromine by chlorine favours electron availability at the *para*-position. Baker (*J. Chem. Soc.*, 1933, 1128) found similar results with aniline and pyridine with *p*-chloro- and *p*-bromobenzyl bromides. On the whole, therefore, the balance of evidence is in favour of the view that the replacement of bromine by chlorine helps electron availability at the *para*-position. The racemisation of the acids studied would be expected to be helped by electron recession, that is by decreased availability at the *para*-position. The chloro- and bromo-acids show no difference so that the difference in electron availability apparently fails to make itself felt at the distance of two carbon atoms. Dippy and Wiliams (*J. Chem. Soc.*, 1934, 162) similarly found almost no difference in the dissociation constants of the *p*-chloro- and *p*-bromophenylacetic acids where the ionisable hydrogen is also separated from *para*-carbon atom by two carbon atoms.

The alternating effect of these halogens is bound up with their electromeric effects which cause greater electron availability at the *para*-position than the *meta* and therefore greater reactivity at the *para*-position towards electron-seeking reagents. This conclusion is supported by the results obtained by Olivier (*loc. cit.*) who showed that *p*-chloro and *p*-bromobenzyl chlorides were hydolysed more rapidly than the *meta*-compounds. The reactivity of the chlorine here is generally regarded as helped by electron accession to the CH_2Cl-group and therefore the *para*-halogen atom appears to favour electron accession to that group as compared with the halogen in the *meta*-position. A comparison of the rates of reaction of *m*- and *p*-chloro- and bromoanilines with benzyl bromide and with dinitrochlorbenzene confirms this conclusion; in all cases the *para*-halogenated amine reacts faster than the *meta*-compound. The racemisation of the acids considered would presumably be helped by electron recession and should, therefore, take place faster with the *meta*-halogen derivatives than with the *para*-compounds. This is true of the *m*- and *p*-bromo-acids but not of the chloro-acids. It is possible that the difference is due to the electromeric effect of bromine being greater than that of chlorine. The unshared electrons of the larger atom would be expected to be less firmly held than those of the smaller atom; it is this effect which is responsible for the greater electron availability in the *p*-position to the halogen than in the *m*- and, therefore, the difference in electron availability in the two positions would be expected to be greater in the case of bromine than in

the case of chlorine. This does not, however, explain why the opposite effect is observed in the case of chlorine which in this particular instance behaves as though the electromeric effect is absent. Further work is obviously necesrary to support the superstructure of theory.

Exeprimental.

The acids were prepared and resolved by the methods described by Peacock and Menon (*Proc. Indian Acad. Sci.*, 1934, **1**, 407, 412). $M/300$ g. of each acid was dissolved in 13·25 c. c. of 1·007N-NaOH and made up to 100 c. c. The sodium salt was thus dissolved finally in $N/10$-NaOH solution. The initial rotation of the solution was taken and then it was heated to 100° in a boiling water-bath and samples withdrawn at regular intervals, cooled, and the rotations measured. In all cases the Hg_{yellow} line was used. The results are tabulated below.

Table II.

Racemisation of Na-α-*substituted* β-*phenylpropionates.*

$Ph{\cdot}CH_2{\cdot}CHRCOONa$ in $N/10$-NaOH at 100°.

Time.	R= *p*-$ClC_6H_4CH_2$.	*m*-$ClC_6H_4CH_2$.	*p*-$BrC_6H_4CH_2$.	*m* $BrC_6H_4CH_2$.
	α	α	α	α
0	0·12°	0·10°	0·31°	0·185°
1 hr.	0·078°	0·07°	0·22°	0·102°
2	0·053°	0·055°	0·12°	0·06°
3	0·033°	0·035°	0·058°	0·032°
4	0·020°	0·030°	0·036°	0·020°
8			0·025°	

Table III.

Racemisation of Na-α-*substituted hexoates*

$C_4H_9{\cdot}CH(R){\cdot}COONa$ in $N/10$-NaOH at 100°.

Time.	R=*p*-$BrC_6H_4CH_2$.	$C_6H_5CH_2$.
	α	α
0	0·50°	0·20°
1 hr.	0·45°	0·18°
2	0·46°	0·17°
3	0·45°	0·16°
4	0·44°	0·16°
8	0·42°	0·16°

We have to thank the University of Rangoon for a grant in aid of this investigation which is being continued.

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Received January 16, 1935.

Studies in Salt Activation. Part I. Influence of Neutral Salts on the Enzyme Hydrolysis of Starch.

By K. Venkata Giri and J. G. Shrikhande.

Although it is well known that many enzyme reactions are accelerated or retarded by salts, the mechanism of the effect has not been studied in detail for any particular enzyme A general theory concerning the effect of ions on the activity of enzymes has not yet been developed, besause of the different mechanism of salt action in different cases. The present investigation was, therefore, undertaken with a view to throwing light on the nature of the salt action on the enzymic hydrolysis of starch in particular and other enzymic reactions in general.

The activating effect of neutral salts on the activity of pancreatic amylase under varied conditions has been thoroughly investigated by Sherman and co-workers (*J. Amer. Chem. Soc.*, 1927, **49**, 2596; 1928, **50**, 2529, 2535, 2538) and Willstätter, Waldschmidt Leitz and Hesse (*Z. physiol. Chem.*, 1923, **136**, 143).

Michaelis and Pechastein (*Biochem. Z.*, 1914, **59**, 77) have investigated the nature of salt activation of salivary amylase. They observed that the diastase is inactive in the complete absence of salts and it combines with all the salts to form double compounds, each of which having very characteristic properties, depending upon the anion of the salt. Each of these complex compounds has diastatic action but differs (*a*) through the affinity of the salt (or anion) for the diastase, (*b*) by the degree of their activity upon the starch (or the affinity of the complex salt-diastase compound for starch), and (*c*) by the acid dissociation constant and on the position of the isoelectric point and the H-ion of its optimum activity upon starch. Ths isoelectric point of all the salt complexes was found to be between 10^{-5} and 10^{-6}, and the optimum activity for PO_4, AcO, SO_4 was *p*H 6·1 to 6·2; for Cl and Br, 6·7; and for NO_3, 6·9.

Contrary to the observations of Michaelis and Pechastein, (*loc. cit.*) Myrbäck (*Z. physiol. Chem.*, 1926, **159**, 1) observed that salivary amylase is active even in absence of salts. The salt and one of its ions, com-

bined with the enzyme and the amylase-salt complex thus formed, was found to be more active only in its undissociated or isoelectric form. Combination with a salt altered the degree of dissociation of the enzyme, thus changing the proportion of the enzyme in the active form at any given *p*H.

There is, however, much controversy regarding the action of neutral salts on vegetable amylases. Some workers observed activation, *viz*,. Eadie (*Biochem. J.*, 1926, **20**, 1016), with barley malt amylase, at salt concentration of 1·62*N*; Patwardhan and Norris (*J. Indian Inst. Sci.*, 1928, **11A**, 127) with cholum malt diastase; Narayanamurthy (*ibid.*, 1930, **13A**, 63) with cholam malt amylase at 0·00016*N*-salt concentration; Sherman Caldwell and Cleaveland (*J. Amer. Chem. Soc.*, 1930, **52**, 2406) with barley malt amylase at an unfavourable H-ion concentrations, and Lisbonne (*Soc. Biol.*, 1912, **72**, 936) with electrodialysed malt amylase; and some others noticed inactivation or no effect in presence of salts.

Fricke and Kaja (*Ber.*, 1925, **57**, 310, 313) observed inactivation with electrodialysed barley malt amylase; Narayanamurthy and Norris (*J. Indian Inst. Sci.*, 1928, **11A**, 104) noted inactivation with electrodialysed cholam malt diastase; Karmakar and Patwardhan (*ibid.*, 1930, **13A**, 159) with wheat amylase observed no effect.

Some interesting observations on salt action have been made with potato amylase by Haen and Schweigart (*Biochem. Z.*, 1923, **143**, 516) who separated an almost free and inactive amylase by dialysis and ultra-filtration which could be activated by salts and amino-acids. Very recently James add Cattle (*Biochem. J.*, 1933, **27**, 1805) working with potato amylase observed that the enzyme responsible for the immediate breakdown of starch molecule to form 'dextrins' is capable of activation by potassium chloride, while another enzyme responsible for the production of sugar from the dextrin, produced by the first enzyme is incapable of such activation.

The foregoing observations by several workers point out the need for further systematic work on the subject. The contradictory results obtained by foregoing authors and several others are chiefly due to the fact that the *p*H of the reaction mixture was neither controlled nor observed. Even in those cases, where the *p*H had been controlled by the addition of buffers, the effect of these buffer salts on the activity of the enzyme, which sometimes depends on their concentrations, had not been thoroughly investigated. A systematic investigation of the problem with all the necessary experimental precautions seemed, therefore, the only means of reaching a satisfactory solution.

Experimental.

Preparation of the enzyme.—Preparations of the amylase were obtained from sweeet potato by the following three different methods, (*i*) by the alcohol precipitation from a direct aqueous extraction of the dried sweet potato meal as described by Venkata Giri (*J. Indian Chem. Soc.*, 1934, **11**, 339), (*ii*) by ordinary dialysis in collodion bags of the aqueous extract of the meal at -1 to $+1°$ temperature in a cold room, (*iii*) by adsorption on alumina gel, elution, and dialysis, a method developed by Giri (*Biochem. Z.*, 1934, **275**, 106) for the purification of the enzyme.

Methods of procedure.—The activity of the enzyme was measured as described in the previous communication. In experiments in which the reaction was to be carried in the presence of neutral salts, the latter were added from the stock solutions to the reaction mixture, the concentration of the neutral salt present in the total volume of reaction mixture (100 c.c.) is expressed as molar concentration.

The hydrogen-ion concentrations of the substrates were adjusted by sodium acetate and acetic acid buffer of a total concentration of 0·04*M*-acetate. For higher ranges of *p*H values, phosphate buffer was used. Soluble starch (Zulkowsky's) was used as substrate.

All the salts employed in the present investigation were of the highest grade of purity, either Merck's or Kahlbaum's guaranteed analytical reagents.

The degree of acceleration of the hydrolysis produced by the neutral salts is always expressed as percentage acceleration, (*A*) which is calculated from the formula

$$A = \frac{(y-x)\ 100}{x}$$

where x denotes the activity of the enzyme in absence of salt, y, the activity of the enzyme in presence of salts. In this way, the results of all the series were made quantitatively comparable.

The Influence of the Concentration of Acetic Acid-acetate Buffer of Varying H-ion Concentrations on the Hydrolysis of Starch.

Reaction mixture containing 100 c. c. of 1% starch and buffer of varying concentrations and *p*H were prepared. The H-ion concentrations of the substrates were adjusted by sodium acetate-acetic acid buffer of total concentration of 0·04*M*, 0·08*M* and 0·12*M*-acetate. The temperature of the reaction mixture was 30°. The enzyme

solution was prepared by dialysis of the aqueous extract of the powder. 5 C. c. of the enzyme solution were used for each hydrolysis experiment. The results are presented in Table I. In the following table k denotes the activity and (A), the percentage acceleration.

TABLE I.

	Buffer concentration (activity $k \times 10^3$).		
p_H.	0·04*M*.	0·08*M*.	0·12*M*.
2·8	12·06	1·2	0
4·0	17·90	3·5	1·2
4·5	20·10	19·8	3·2
5·6	29·40	30·1	29·4
6·0	30·40	30·4	30·8
6·5	25·60	25·6	26·6

The figures indicate that at high concentrations of 0·08*M* and 0·12*M* and at p_H more acid to the optimum, the hydrolysis is very much depressed by the buffer. But at p_H 5·6 to 6·0, which is the optimum one for the enzyme, and on the alkaline side of the optimum p_H, the concentration of buffer has no influence on the enzymic hydrolysis of starch. Hence, to avoid the adverse effect of buffer salt, the hydrolysis experiments were always carried at low concentrations of buffer (0·04*M*). The H-ion concentrations of the substrates were always, therefore, adjusted to a total concentration of 0·04*M*-acetate.

Influence of Neutral Salts at Varying H-ion Concentrations on the Enzymic Hydrolysis of Starch.

The influence of neutral salts upon the activity of the amylase was studied at three different H-ion concentrations, *viz.*, optimum p_H (6·0), acid side of optimum p_H (4·0), and alkaline side of optimum p_H (8·0), in presence of 0·1*M* concentration of the salts. In the case of sodium chloride, the activity of the amylase was sudied in the presence of 0·1*M* and 0·5*M* concentrations of the salt at closely graded H-ion activities from p_H 2·7 to 8·0.

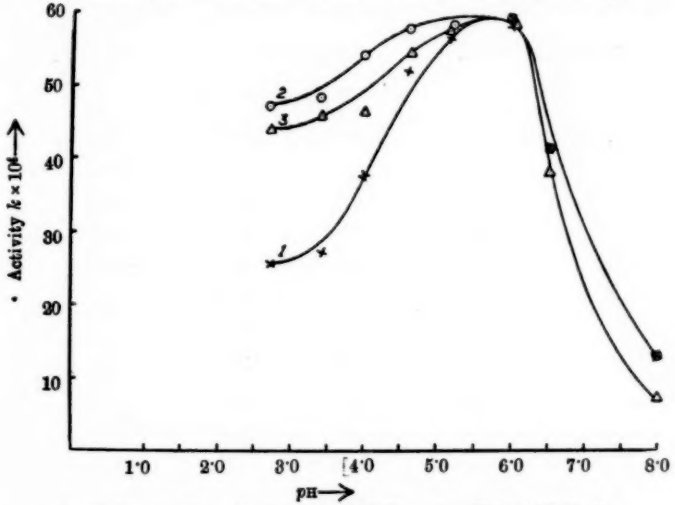
The reaction mixtures consisted of 2% starch, buffer of varying p_H present in a total concentration of 0·04*M*-acetate and salt, the total volume of the reaction mixture amounting to 100 c.c. including the quantity of the enzyme added. The enzyme preparation used for

these experiments was obtained by precipitation with alcohol from the aqueous extract of the powder. The hydrolysis was carried at 30°.

The results are presented in Tables II and III and graphically represented in Fig. 1. It will be seen from the results that sodium chloride in the region of p_H, 5·6 to 6·0 and sodium fluoride, sodium nitrate and sodium sulphate at p_H, 6·0 are without effect on the activity of the amylase. This region corresponds to the region of optimum p_H which has been previously established for the enzyme. On comparing the activity of the enzyme in presence of 0·1*M* sodium chloride and in its absence at p_H 2·7 to 4·6, the activity is greater in its presence, the percentage of acceleration increasing towards the more acid region. Thus, it can be seen from Table I, that the percentage of acceleration at p_H, 4·6 is 11·2 which increases with rise in the acidity and finally reaching a maximum acceleration of 84·4 at p_H 2·7. On increasing the concentration of sodium chloride to 0·5*M*, the acceleration is decreased.

FIG. 1

Influence of NaCl *on the activity of amylase at different* p_H.



1. Without salt. 2. With 0·1*M*-NaCl. 3. With 0·5*M*-NaCl.

The activity of the amylase is unaffected with 0·1*M*-NaCl, but is considerably depressed with 0·5*M*-NaCl in the range of p_H, 6·5 to 8·0.

The influence of sodium fluoride, sodium nitrate and sodium sulphate was studied in the same way as that of sodium chloride but the

influence of these salts was measured only at p_H 4·0, 6·0 and 8·0. A similar acceleration was observed at p_H 4·0 in the presence of these salts, and at its optimal hydrogen-ion concentration the amylase was as active without as with the neutral salts. At p_H 8·0, however, the activity of the enzyme is not affected by the presence of the salts. Sodium sulphate, however, depresses the activity at p_H 8·0. It is probable that the depressing effects of these salts in the alkaline region may be pronounced when the concentration of the salts is increased.

Thus the amylase shows optimal action through a wide range of H-ion concentration in presence of neutral salts. The foregoing results point out the need for controlling the H-ion concentration of the reaction mixture when the effect of neutral salts on the activity of amylase is to be studied. Further, these observations explain the contradictory results obtained by several workers when studying the influence of neutral salts on the activity of vegetable amylases.

TABLE II.

Starch conc. = 2%. Amylase conc. = 0·01%. Salt conc. = 0·1*M*.

NaCl conc.	p_H	Activity $k \times 10^4$		(*A*).
		with NaCl.	without NaCl.	
0·1*M*	2·7	47·2	25·6	84·4%
	3·4	48·1	27·2	76·9
	4·0	54·2	37·3	45·3
	4·6	57·6	51·8	11·2
	5·6	55·6	56·0	−0·7
	6·0	58·3	58·3	0
	6·5	41·0	41·0	0
	8·0	10·3	10·3	0
	2·7	40·4	25·6	58·0
	3·4	45·4	30·7	48·0
	4·0	45·9	37·3	23·0
	4·6	54·7	53·9	1·5
0·5*M*	5·6	57·7	57·7	0
	6·0	58·3	58·3	0
	6·5	38·5	41·0	−6·1
	8·0	7·1	10·6	−33

TABLE III.

Strach conc. = 2%. Amylase conc. = 0·01%. Salt conc. = 0·1*M*.

		with NaF		Na_2SO_4		$NaNO_3$	
p_H.	$k \times 10^4$ without salt.	$k \times 10^4$.	(*A*)	$k \times 10^4$.	(*A*).	$k \times 10^4$.	(*A*).
4·0	36·0	54·6	51·7%	51·6	43·0%	48·9	35·8%
6·0	57·2	57·2	0	57·2	0	57·5	0·5
8·0	10·3	10·3	0	8·5	−17·4	10·2	0

Influence of Varying Concentrations of Neutral Salts on the Enzymic Hydrolysis of Starch.

The activity of the amylase in presence of varying concentrations (0·001*M* to 0·50*M*) of neutral salts and in their absence at p_H 4·0 was measured. The reaction mixtures consisted of 2% starch, acetic acid-acetate buffer of p_H 4·0 and salts of varying concentrations, the total volume of the reaction mixture amounting to 100 c.c. The results are presented in Table IV.

TABLE IV.

Starch conc. = 2·0 %. Amylase conc. = 0·01%. p_H = 4.

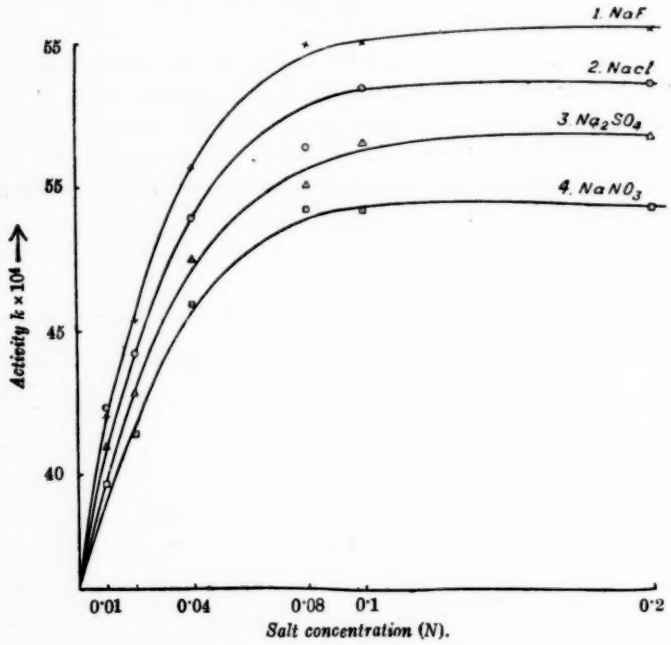
	NaF.		NaCl.		Na_2SO_4.		$NaNO_3$.	
Salt conc.	$k \times 10^4$.	(*A*).	$k \times 10^4$.	(*A*).	$k \times 10^4$.	(*A*).	$k \times 10^4$.	(*A*).
0	36·0	...	36·6	...	36·6	...	36·6	...
0·001*N*	36·0	0	36·6	0	36·6	0	36·6	0
0·01	42·0	16·2%	42·3	15·6%	41·0	12·9%	39·7	8·5%
0·02	45·3	26·0	44·2	20·8	42·8	17·0	41·4	13·1
0·04	50·6	40·6	48·9	33·6	47·5	30·0	45·9	25·4
0·08	54·9	52·5	51·3	41·5	50·0	36·6	49·1	34·1
0·10	54·9	52·5	53·3	45·6	51·5	40·8	49·1	34·1
0·20	55·2	53·3	53·3	45·6	51·6	40·8	49·1	34·1

The figures in Table IV show that the activity of the amylase increases with the increase in the concentration of neutral salts, reaching a maximum at salt concentration of about 0·10 − 0·20*M*. On

comparing the maximum acceleration of activity attained in presence of each salt, it can be seen that the activity varies with different salts. The results are shown graphically in Fig. 2. It can be seen that the curve corresponding to each salt is approximately a rectangular hyperbola, suggesting according to Michaelis' theory, that the salt probably combines with the enzyme to give a more active enzyme-salt complex. These salts can be arranged as follows according to the decreasing magnitude of their effects on the activity of the amylase at p_H 4·0: $NaF < NaCl < Na_2SO_4 < NaNO_3$.

FIG. 2.

Influence of varying concentrations of salt on the activity of the amylase at pH 4·0.



The Influence of Cation on the Acceleration of the Enzymic Hydrolysis of Starch.

Reaction mixtures containing 1 % starch and a total concentration of 0·1*M* of the salts in a total volume of 100 c.c. were prepared and

the activity determined. The hydrolysis was carried at p_H 6·0 and 4·0 at 30° and the results are given in Table V.

TABLE V.

Neutral salt.	p_H.	$k \times 10^3$.	p_H.	$k \times 10^3$.
Control	4·0	19·0	6·0	34·1
LiCl	4·0	32·7	6·0	34·2
NaCl	4·0	34·8	6·0	35·0
KOl	4·0	32·2	6·0	36·0
$CaCl_2$	4·0	34·0	6·0	36·1
$BaCl_2$	4·0	34·2	6·0	36·4

The above results indicate that the cations of the salts investigated have no influence on the activity of the amylase. A similar observation was made by Norris (*Biochem. J.*, 1913, 7, 626) in the case of the hydrolysis of glycogen by pancreatic amylase. Cole (*J. Physiol.*, 1906, 30, 202) however, considered that the anion accelerated while kation depressed the action. If the latter were correct, the chlorides containing a bivalent cation should be less active than sodium or potassium chloride. The above results, as well as the observations of Norris (*loc. cit.*), suggest that such is not the case. The view that the anion is the more important factor in the acceleration of the hydrolysis of starch, is further strengthened by taking into account the relative accelerating power of flouride, chloride, sulphate and nitrate.

Influence of Concentration of the Enzyme on tha Accelerating Effect of NaCl.

A series of mixtures were made up each containing 2 per cent. starch and a concentration of sodium chloride ranging from 0 to 0·20*M*, the p_H of the substrate being adjusted to 4·0. When the concentration of the enzyme was 1 c.c., the aliquots were taken out at intervals of 20, 40 and 50 minutes, and at shorter intervals of 5, 10, and 15 minutes, when the concentration of the enzyme was increased to 2 and 4 c.c. The results are presented in Table VI.

TABLE VI.

Conc. of NaCl.	Quantity of the enzyme. 1 C.c. $k \times 10^4$.	(A).	2 C.c. $k \times 10^4$.	(A).	4 C.c. $k \times 10^4$.	(A)
0	18·8	...	36·8	...	74·5	...
0·001 *M*	18·8	0	36·8	0	74·6	0
0·002	20·9	11·2%	39·3	6·9%	27·7	4·3%
0·003	21·1	12·1	42·6	10·3	80·1	7·5
0·005	22·0	17·0	41·9	13·9	82·0	10·0
0·01	22·8	21·3	42·2	16·3	84·2	13·0
0·02	24·1	28·2	46·5	26·3	90·9	22·0
0·06	27·3	45·2	53·6	45·6	108·0	45·0
0·10	27·3	45·2	53·6	45·6	108·0	45·0
0·20	27·3	45·2	53·6	45·6	108·0	45·0

It can be seen from the results that the percentage of acceleration in presence of the salt, below a concentration of 0·02*M* varies inversely as the concentration of the enzyme. When the salt concentration exceeds 0·02*M* the accelerating action of the salt is independent of the enzyme concentration.

Influence of Substrate Concentration on the Accelerating Effect of NaCl.

A series of reaction mixtures containing 1, 2 and 3% of starch and of varying concentrations of NaCl were prepared, and the extent of hydrolysis was determined by allowing the hydrolysis to proceed at 30° for 15 minutes and estimating the maltose formed in the total volume (100 c.c.) of the reaction mixture. The p_H of the substrate was adjusted to 4·0. The results are shown in Table VII.

It can be seen from figures in Table VII that the accelerating effect of NaCl depends also on the concentration of starch, the higher the concentration of starch, the less is the acceleration produced by salt at the same salt concentrations.

TABLE VII.

Starch concentration.

Conc. of NaCl.	1 %.		2 %.		3 %.	
	Maltose.	(A).	Maltose.	(A).	Maltose.	(A).
0·	135 mg.	...	171 mg.	...	198 mg.	...
0·02 *M*	162	20·0%.	203	18·8%	230	16·2%
0·04	185	37·0	225	31·1	237	18·2
0·10	212	56·8	234	37·0	243	22·7
0·20	212	56·6	230	34·5	239	20·7

Influence of the Purity of the Enzyme on the Accelerating Effect of Salts.

Since it might be expected that the salt acceleration, if a property of the enzyme itself and not of the impurity associated with it, would be characteristic and invariant, it was found necessary to investigate the phenomenon with more than one preparation of the enzyme subjected to various forms of treatment.

Enzyme preparation (A).—Prepared by alcohol precipitation from the aqueous extract of the dry powder. The concentration of the enzyme used was 0·01 %.

(B). Prepared by dialysis of the aqueous extract. 5 C.c. of the enzyme solution were used for each determination.

(C). Prepared by adsorption on alumina gel, elution and dialysis (Giri, *loc. cit.*).

The following is a brief description of the method adopted for the purification of the enzyme:—100 G. of the powder were extracted with 600 c.c. of water for 2 hours at the laboratory temperature and filtered. The filtrate was then centrifuged and dialysed in collodion bags in cold room at $-1°$ to $+1°$ for 4 days. 500 C.c. of the dialysed solution were mixed with 100 c.c. of acetic acid-acetate buffer ($M/5$) of p_H 3·7, and 10 c.c. of alumina gel (0·178 g. of Al_2O_3) and kept for 10 minutes with frequent shaking. It was then centrifuged and the adsorbate was eluted with 300 c.c. of $M/75$-phosphate buffer at p_H 7·1 with frequent shaking for about 2 hours in a refrigerator and again centrifuged. The phosphate present in the centrifuge was removed by precipitation with magnesia mixture and the precipitate thus

formed was immediately filtered and the filtrate was neutralised with acetic acid. All these operations were carried at low temperature. The solution thus obtained was dialysed for 3 days in cold room and the enzyme solution thus purified was used for the following experiment.

TABLE VIII.

2% NaCl = 0·1*M*.

	Precipitation A.			Precipitation B.			Precipitation C.		
	$k \times 10^4$.			$k \times 10^4$.			$k \times 10^4$.		
p_H.	without salt.	with salt.	(*A*).	without salt.	with salt.	(*A*).	without salt.	with salt.	(*A*).
4·0	36·1	53·0	46·8%	30·2	44·0	45·7%	39·0	56·5	45·0%
6·0	58·1	58 1	0	46·3	46·3	0	60·5	60·6	0
8·0	10·2	10·2	0	9·1	9·1	0	11·3	11·3	0

The results indicate that NaCl behaves in the same manner with all the enzyme preparations, showing thereby that the accelerating effect of the salt is essentially a property of the enzyme.

DISCUSSION.

The question whether neutral salts accelerate the hydrolysis of starch by the amylase, depends upon the H-ion concentration of the medium, and also upon the concentration of neutral salts. By suitably varying these two factors, acceleration, retardation, or no effect can be found. Thus the results in Tables II and III indicate that salts are capable of accelerating the velocity of hydrolysis of starch to an extent dependent upon the p_H of the medium. At p_H higher than the optimum (p_H 6·0) the reaction is retarded at high salt concentration, whilst below p_H 6·0 it is accelerrted to an extent proportional to the acidity of the system.

H-ion determinations made by colorimetric method on starch solutions containing varying concentrations of neutral salts show that the reaction of the medium is not altered by the presence of salts in the concentrations employed. The p_H of the reaction mixture also remains unaltered during the course of hydrolysis. Hence the accelerating effect of neutral salts is not due to the above cause.

In order to explain the mechanism of salt acceleration the following possibilities may be considered:

Activation of the enzyme by the salts may be brought about either by

(1). (*a*) Altering its colloidal properties or (*b*) combining with the enzyme molecule to form compounds possessing different properties.

(2). By protection of the enzyme against heat inactivation or from inhibiting substances formed during the reaction.

Considering the possibility that salts may accelerate the hydrolysis of starch by altering the colloidal properties, a change in the degree of dispersion of the enzyme in presence of salts and as well as a change in the isoelectric point of the enzyme (Haehn and Harpuder, *Z. Biol.*, 1920, **71**, 302) are the factors to be taken into consideration in such studies. But in some cases the effect is so specific that no general theory can be offered.

It has been shown that anions are more concerned in the acceleration than kations. As to the reason for the variations produced by the anions, some change in the colloids, either of the starch or the enzyme or both, suggests itself. In the present investigation, it has been shown that the degree of accelerating effect of salts is dependent on the concentration of starch and of the enzyme. This suggests that the effect produced may be due to some changes in the enzyme and the substrate molecule. No definite evidence is so far available with regard to the nature of such a change. In the action of amylase on starch, both the substrate and the enzyme are colloids, and hence it is likely that the action of salts may not only be confined to the enzyme. In certain cases, however, where the substrate is not a colloidal solution, the influence of salts may be chiefly confined to the enzyme. Thus, the observations made by Cole (*J. Physiol.*, 1906, **30**, 281) that in the action of invertase, where the substrate is not a colloidal solution, salts have a powerful influence (in this case the hydrolysis is retarded by chloride), it is probable that the action of the salts is chiefly confined to the enzyme. It is, therefore, desirable to study separately the effect of salts on starch and enzyme from the point of view of adsorption and charge.

In this connection it may be of interest to mention the work of Biedermann (*Biochem. Z.*, 1923, **135**, 282; **137**, 35) whose results led to the following generalisations; of all the components of a system which apparently contains a diastatic enzyme, only the inorganic salt or its ions are able in association with oxygen to break down starch with the formation of sugar. The organic compounds are unable to effect this unless salts and oxygen are present. Thus the decomposition

tendency of the substrate in presence of neutral salts is another point to be considered in studies on salt activation.

Regarding the other possibilities it is likely that either the salts combine with the enzyme molecule to form compounds possessing different properties or that the salts accelerate the hydrolysis of starch by protecting the enzyme against inactivation or from inhibiting substance produced during the reaction. Further experiments are in progress to test the above hypothesis.

Summary.

1. The effect of neutral salts like sodium fluoride, sodium chloride sodium sulphate and sodium nitrate on the hydrolysis of starch by the sweet potato amylase has been studied under varied conditions.

2. The salts accelerate the action of the amylase at p_H higher than 6·0, in presence of high salt concentration. Sodium chloride accelerates the activity at p_H below the optimum to an extent increasing with the acidity of the medium. At p_H 6·0, the activity of the enzyme is not affected by the presence of salts.

3. The accelerating effect of all the neutral salts at p_H 4·0 is found to increase with the increase in concentration of the salt, and the effect is lessened on further increase.

4. The salts may be arranged according to the decreasing magnitude of their effect on the activity of the amylase at p_H 4·0.
Sodium fluoride ∠ sodium chloride ∠ sodium sulphate ∠ sodium nitrate.

5. The accelerating effect of sodium chloride on the enzymic hydrolysis of starch is influenced by the concentration of the enzyme and of the substrate.

6. The accelerating effect of salts is essentially a property of the enzyme.

7. Various possible theories to explain the salt activation have been indicated and discussed.

The author's thanks are due to Prof. V. Subrahmanyan, for his keen interest in the work.

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REVIEW

Kolloid Chemie der Seifen. By Dr. E. L. Lederer, Hamburg. Published by Theodor Steinkoppf, Dresden and Leipzig, 1932. Pp. 430 + XVI. Price 38 R. Marks.

The book under review is Vol. 5 of the Handbuch der Kolloidwissenschaft in Einzeldarsteilungen, edited by Prof. Dr. Wolfgang Ostwald. In keeping with the thoroughness of the other volumes, this volume gives us within 430 pages an up to date summary of the experimental work on soaps. The book gives a very lucid exposition of main results of technical and theoritical significance. There are six main chapters including a short introduction as follows: Properties of Pure soaps; Behaviour of Soaps in presence of Electrolytes ; Their Detergent Properties; The Colloid Chemistry of the Technical Saponification and Soap formation Processes ; Metal Soaps and Substances resembling Soaps. Both the technician and those interested in the study of or in research on soap systems will find the book very helpful. The critical comments of the author are well balanced and no particular stand point has been either overlooked or overemphasised.

J. N. M.

Einfuhrung in die Lehre von den Kolloiden. Edited by Prof. Dr. H. Bechhold. Published by Theodor Steinkoppf, Dresden and Leipzig, 1934. Pp. 160 + VIII.

The volume is the result of the co-operative efforts of several authors including Prof. Bechhold. It is a collection of short accounts on selected topics dealing with colloids. The subjects discussed are: What are Colloids ; Preparation of colloidal solution; The Colloidal particles as Physical molecules ; Interfaces and Interfacial Reactions ; Sol, Gel and Coagula; Electric properties of Colloid system, Separation and Purification of Colloids; Optical properties of Colloids and Investigation of Colloids with X-Rays. The book is neither a text book nor a monograph nor a review. The presentation of some of the facts appears to have been rather one-sided and may lead to misconception. The numerous figures will be found very helpful. An attempt has been made to cover a wide range under each chapter. Inspite of the restrictions imposed by the plan of the book it will be found helpful as it deals with many aspects of the subjects which do not ordinarily find a place in the shorter treatises.

J. N. M.

Synthesis in the Pyridine Series.

By Umaprasanna Basu.

It has been recently shown (Basu, *Annalen*, 1934, **512**, 131; 1934, **514**, 292) that the condensation of different 2-hydroxymethylene *cyclo*hexanones with tautomeric compounds of the ketimine-enamine type, $HN:CR\cdot CH_2X \rightleftharpoons H_2N\cdot CR:CH\cdot X$ ($X = CO\cdot R$, CO_2R, etc.), gives rise to various *Bz*-tetrahydroquinolines. Substituting the cyclic ketone derivatives by hydroxymethylene compounds (I) derived from open-chain ketones, it would be possible to effect syntheses of numerous pyridine derivatives (II) having a negative substituent at the β-position (*cf.* Späth, *Monatsch.*, 1928, **49**, 266) thus:

(I) (II)

Accordingly, hydroxymethylene compounds obtained from ethyl-phenylketone, *p*-methylacetophenone and methylethylketone were treated with ethyl β-aminocrotonate, when from the reaction products ethyl 2:5-dimethyl-6-phenyl-, 2-methyl-6-*p*-tolyl- and 2:5:6-trimethyl-pyridine-3-carboxylates were respectively obtained. All these pyridine-β-carboxylates are basic substances easily soluble in dilute acids and form additive compounds with picric acid. They are insoluble in water but readily dissolve in ether, alcohol and other common organic solvents. On hydrolysis with caustic potash solution they give the corresponding pyridine-β-carboxylic acids, which are easily soluble in water, alcohol and chloroform, difficultly in ether and acetone and sparingly in petroleum ether. They exhibit the character of amino acids and impart no colouration to ferrous sulphate solution.

In the light of these observations, it appeared probable that by using an enamine compound of the type $R'CO{\cdot}CH{:}CRNH_2$, a method for the synthesis of β-pyridyl alkyl or aryl ketones might be found. A preliminary condensation in this direction has been brought about between benzoylacetoneamine, $PhCO{\cdot}CH{:}CMeNH_2$ and hydroxymethylene *p*-methylacetophenone. From the experimental results so far obtained there are reasons to believe that the product of reaction is 2-methyl-6-*p*-tolyl-3-benzoylpyridine [II, R=Me, R′=(*p*) $Me{\cdot}C_6H_4$ and X=CO·Ph].

Experimental.

Hydroxymethylene ethylphenylketone and ethyl β-aminocrotonate: Formation of ethyl 2:5-dimethyl-6-phenylpyridine-3-carboxylate.—15 G. of the hydroxymethylene ketone, prepared according to the method of Claisen and Meyerowitz (*Ber.*, 1889, **22**, 3275), m.p. 118-19° on crystallisation from alcohol, was dissolved in ether and mixed with ethyl β-aminocrotonate (12 g.). The solution was then heated under reflux on a water-bath for about 15 hours. The ether was driven off and the residual mass was treated with dilute hydrochloric acid when a resinous mass separated out. This was filtered off and the clear acid filtrate was neutralised with sodium carbonate. The oil separating, was extracted with ether, ethereal solution dried over anhydrous sodium sulphate and the ether evaporated off. The remaining liquid on distillation at 170-185°/8mm. yielded a solid (12 g.) which on crystallisation from dilute alcohol melted at 59°. (Found: N, 5·56. $C_{16}H_{17}O_2N$ requires N, 5·49 per cent.).

Picrate.—The pyridine carboxylate derivative on treatment with an alcoholic solution of picric acid yielded a picrate which on crystallisation from alcohol was obtained in yellow rectangular prisms, m.p. 146°. [Found: N, 11·73. $C_{16}H_{17}O_2N$, $C_6H_2(NO_2)_3OH$ requires N, 11·57 per cent].

Hydrolysis: Formation of 2:5-dimethyl-6-phenylpyridine-3-carboxylic acid.—The above pyridine carboxylate (6 g.) was refluxed with 24 c.c. of caustic potash solution (15%) till a clear solution was obtained. This was then acidified with hydrochloric acid (to Congo paper) and evaporated to dryness on a boiling water-bath. The whole mass was extracted with chloroform. The chloroform solution was then concentrated (after charcoaling) and diluted with petroleum ether

when the carboxylic acid was precipitated out. This was collected and crystallised from a mixture (1:1) of the above two solvents in shining flakes, m.p. 140° (decomp.) (Found: N, 5·85. $C_{14}H_{13}O_2N$ requires N, 6·17 per cent).

Hydroxymethylene p-*methyl*-1-*acetophenone and ethyl* β-*aminocrotonate*: *Formation of ethyl* 2-*methyl*-6-p-*tolylpyridine*-3-*carboxylate*.—The hydroxymethylene derivative of *p*-methylacetophenone was prepared according to Benary, Meyer and Charisius (*Ber.*, 1926, **59**, 108) and preserved as its sodium salt. The oxymethylene compound was freshly liberated from the above salt before use. Thus 18 g. of the sodium salt were decomposed with dilute acetic acid and the liberated oxymethylene compound was extracted with ether. The ethereal solution was then heated with ethyl β-aminocrotonate (12 g.) for about 15 hours. The ether was then evaporated off and the reacted mixture was treated as in the previous case, when the hydrochloric acid solution on neutralisation gave a solid product. This on crystallisation from dilute alcohol was obtained in fine scales, m.p. 54°. (Found: N, 5·60. $C_{16}H_{17}O_2N$ requires N, 5·49 per cent).

The *picrate* of the above pyridine derivative was prepared as usual and found to crystallise out from alcohol, m.p. 133°. [Found: N, 11·55. $C_{16}H_{17}O_2N$, $C_6H_2(NO_2)_3OH$ requires N, 11·57 per cent].

Hydrolysis: *Formation of* 2-*methyl*-6-p-*tolylpyridine*-3-*carboxylic acid*.—This was prepared by heating the ester (3 g.) with 12 c.c. of caustic potash solution till a clear solution was obtained. The solution was made acid to Congo paper and evaporated to dryness. Extracting the mass with absolute alcohol and then concentrating the alcoholic solution, the carboxylic acid crystallised out in shining tiny crystals, m.p. 207-8° with decomposition. (Found: N, 6·04. $C_{14}H_{13}O_2N$ requires N, 6·17 per cent).

Hydroxymethylene butanone ($Me{\cdot}CO{\cdot}CMe{\cdot}CHOH$) *and ethyl* β-*aminocrotonate*: *Formation of ethyl* 2:5:6-*trimethylpyridine*-3-*carboxylate*.—12 G. of the hydroxymethylene ketone, obtained from methylethylketone according to the method described by Benary, Meyer and Charisius (*loc. cit.*; *cf.* Benary, *Ber.*, 1926, **59**, 600), and ethyl β-aminocrotonate (15 g.) were mixed together and the mixture was heated on a boiling water-bath for more than 6 hours. The reaction product on subsequent treatment as usual yielded an oil (9 g.), b.p. 134-36°/11 mm. (Found: N, 7·52. $C_{11}H_{15}O_2N$ requires N, 7·25 per cent).

This pyridine carboxylate derivative is a yellow refracting liquid, $n_{31}^{\circ}=1{\cdot}5056$. It distills at 256-57°/755 mm. It is insoluble in water but dissolves readily in common organic solvents.

The *picrate*, on crystallisation from alcohol, melts at 157°. [Found: N, 13·39. $C_{11}H_{15}O_2N$, $C_6H_2(NO_2)_3OH$ requires N, 13·27 per cent].

A salt was also prepared by adding the pyridine carboxylate to an alcoholic solution of mercuric chloride. It crystallised from alcohol diluted with a few drops of water as fine needles, m.p. 118·5°. The salt is being regarded as $C_{11}H_{15}O_2N$, $HgCl_2$.

Hydrolysis: *Formation of 2:5:6-trimethylpyridine—3-carboxylic acid.*—The acid was prepared as usual by hydrolysing the ester with caustic potash solution. It was obtained in shining needles from alcohol, m.p. 217-18° (decomp.). (Found: N, 8·07. $C_9H_{11}O_2N$ requires N, 8·48 per cent).

Hydroxymethylene p-methylacetophenone and benzoylacetonamine.—About 4 g. of the former substance were heated with a molecular proportion of benzoylacetonamine in alcoholic solution. On adding dilute hydrochloric acid to the reaction mixture benzoylacetone was found to separate out. The acid filtrate, however, on neutralisation with sodium carbonate afforded a thick oil which readily gave a picrate with an alcoholic solution of picric acid. This on crystallisation from alcohol was obtained in bright yellow prismatic needles, m.p. 191°. The percentage of nitrogen present in the compound was found to be 10·31. The picrate [$C_{20}H_{17}ON$, $C_6H_2(NO_2)_3OH$] of 2-methyl-6-*p*-tolyl-3-benzoylpyridine, the expected product of reaction between hydroxymethylene *p*-methylacetophenone and benzoylacetonamine, requires N, 10·85 per cent.

Further work in this direction is in progress. In conclusion, the author wishes to express his sincere thanks to Prof. H. K. Sen for placing the resources of his laboratory at his disposal.

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Studies on Azo-aldehydes.

By Rajendra Nath Sen and B. N. Banerji.

The azo-aldehydes form an interesting group of compounds on account of the fact that they may be used as intermediate products in the synthesis of beautiful and useful dyes with multiple chromophores (Green and Sen, *J. Chem. Soc.*, 1912, **101**, 1113; Sen and Sett, *J. Amer. Chem. Soc.*, 1924, **46**, 111; Dutt, *J. Chem. Soc.*, 1926, **129**, 1171; Sen and Ghosh, *J. Indian Chem. Soc.*, 1928, **5**, 487; Sen and Sen, *ibid*, 1930, **7**, 151).

The possibility of preparing hydroxy-azo-aldehydes by Reimer and Tiemann's reaction appears not to have been fully investigated. The only attempt made in this direction appears to be that of Borsche (*Ber.*, 1900, **33**, 1925) and of Borsche and Bolsten (*Ber.*, 1901, **34**, 2094) who obtained benzeneazo-salicylaldehyde and benzeneazo-*o*-cresolaldehyde respectively from the corresponding hydroxy-azo compounds. It, therefore, seemed to be of interest to study the hydroxy-azo-compounds further with a view to derive from them the dyes with multiple chromophores.

The chief difficulty in the preparation of hydroxyazo-aldehydes by Reimer and Tiemann's reaction is due to the fact that most of the hydroxyazo compounds generally are not very soluble in concentrated caustic soda solution, the sodium salts of the azophenols being invariably precipitated. Consequently a comparatively dilute solution (23%) of caustic soda has to be taken which accounts for the rather low yield obtained in these cases. It has been found that a mixture of chloroform and alcohol (1:4), instead of chloroform alone as in the modified method of Sen and Ray (*J. Indian Chem. Soc.*, 1932, **9**, 173) increases the yield to some extent.

The effect of substituents in the phenol residue and in the benzene residue of the azophenols on the yield of the corresponding aldehydes has also been thoroughly investigated.

The yield of the aldehyde from benzeneazoresorcinol is greater than from benzeneazophenol. The reactivity of the hydroxyazo-compounds with an alkyl radical (Me) in the *ortho*-position to the OH group appears to be more or less diminished; and the reactivity is still further diminished by the presence of one alkyl radical in the *ortho*-position and another alkyl radical in the *meta*-position as in the case of benzeneazothymol and benzeneazocarvacrol. It is remarkable to observe that chlorine in the *o*-position to the OH or a NO_2

group in the *o*-or *m*-position to the OH, inhibits the reaction almost completely. It is observed that substituents generally exert a more or less inhibiting effect, it being more marked when substituting groups are present in the phenol residue as is evident from Table I.

TABLE I.

Substituting groups.	In the benzene residue as.	Yield.	In the phenol residue as.	Yield.
NO_2	*p*-Nitrobenzeneazophenol	7%	Benzeneazo-*m*-nitrophenol	No reaction
	o-Nitrobenzeneazophenol	4	Benzeneazo-*o*-nitrophenol	No reaction
	m-Nitrobenzeneazophenol	5		
Cl	*p*-Chlorobenzeneazophenol	10	Benzeneazo-*o*-chlorophenol	No reaction
	o-Chlorobenzeneazophenol	10		
Me	*o*-Toluneazophenol	8	Benzeneazo-*o*-cresol	4%
	p-Toluneazophenol	8		

With a view to confirm the constitution of the various hydroxyazo compounds, thus obtained, most of them have been further synthesised by diazotising the corresponding amino compounds and coupling with the corresponding hydroxy aldehydes (*vide* Experimental).

The hydroxyazo-aldehydes exhibit marked inactivity in forming bisulphite compounds and in reducing ammoniacal silver nitrate solution. They give semicarbazones and phenylhydrazones with extreme difficulty.

The shades produced on silk by the azo-aldehydes themselves generally differ very little from that of the corresponding azo compounds. It is, however, interesting to observe that the entrance of a CHO group into benzeneazothymol or benzeneazocarvacrol remarkably diminishes the depth of the colour.

It is noted that the introduction of a nitro group into benzeneazosalicylaldehyde in *p*-position to the azo-group as in *p*-nitrobenzeneazo-salicylaldehyde or the introduction of an additional OH group into the molecule as in benzeneazodihydroxybenzaldehyde increases the depth of the colour. Thus, while benzeneazo-salicylaldehyde is yellow, *p*-nitrobenzeneazo-salicylaldehyde is yellowish orange and benzeneazo-dihydroxybenzaldehyde is orange. The entrance of a nitro group into the *ortho*- or *meta*-position to the azo-group or the presence of a Cl in the molecule has little or no effect on the depth of

the colour, the corresponding compounds being all yellow. It is noteworthy that the introduction of Me group into benzeneazo-salicylaldehyde has different effect according as the Me group is in the benzene nucleus or phenol residue. Thus *o*-or *p*-toluneneazo-salicylaldehyde having the Me group in the benzene nucleus produces yellow shade on silk while benzene-azo-*o*-cresol-aldehyde with a Me group in the phenol nucleus produces golden yellow shade.

With a view to study the influence of various substituents, *viz.*, OH, NO_2, Me, etc., some of these azo-aldehydes have been successfully condensed with dimethylaniline and resorcin, beautiful dyes of the azotriphenylmethane and azopyronine series being obtained with the two chromophores in *meta*-position to each other. This will form the subject matter of a separate communication.

Experimental.

Benzeneazoresorcyl aldehyde.—Benzeneazoresorcin (15 g.) dissolved in a mixture of chloroform (50 c.c.) and alcohol (200 c.c.) was added drop by drop with constant stirring to a solution of caustic soda (80 g. in 320 c.c. of water) kept in a flask, fitted with an upright condenser and heated on the water-bath to 60° when the sodium salt of the azo-aldehyde separated out. After stirring for 8 hours the alcohol and the excess of chloroform was distilled off, the sodium salt was collected, dissolved in hot water, and the free hydroxyaldehyde precipitated with acetic acid. Benzeneazoresorcin was separated from the corresponding aldehyde by repeated treatment with large excess of carbon tetrachloride in which the aldehyde is sparingly soluble in cold. It is obtained as micro-crystalline red powder from dilute alcohol, m.p. 231°, yield 3·5 g. It is soluble in chloroform, pyridine, acetone, benzene; sparingly in ether and carbon tetrachloride. It dyes silk with orange shade. (Found: N, 11·63. $C_{13}H_{10}O_3N_2$ requires N, 11·57 per cent).

The aldehyde is identical with the aldehyde prepared by Borsche and Bolsten (*loc. cit.*) by coupling diazotised aniline with β-resorcyl aldehyde, the mixed melting points being identical. The *phenylhydrazone*, prepared in the usual way, crystallises from dilute acetic acid and melts at 217° and is identical with the phenylhydrazone obtained by Borsche and Bolsten (*loc. cit*). (Found: N, 16·92. $C_{19}H_{16}O_2N_4$ requires N, 16·86 per cent).

The other aldehydes prepared are described in the Table II.

TABLE II.

Compound.	Prepared from.	M.p.	Shade on silk.	Analysis. Found.	Calc.	REMARKS.
Benzeneazosalicyl-aldehyde	Benzeneazophenol	127°	Yellow	...	...	Golden yellow prisms from alcohol. Identical with the compound described by Tummley (*Annalen*, 1889, **251**, 17) and Borsche (*loc. cit.*); phenylhydrazone, m.p. 198°.
Benzeneazo-*o*-cresol aldehyde	Benzeneazo- *o*-cresol	76°	Golden yellow	...	...	Brown needles from alcohol; phenyl hydrazone, m.p. 147-48°, identical with the compound, prepared by Borsche and Bolsten (*loc. cit.*).
Benzeneazothymol aldehyde ($C_{17}H_{18}O_2N_2$)	Benzeneazothymol and from diazobenzene chloride and thymol aldehyde (Sen and Roy, *loc. cit.*)	178°	Pale yellow	N, 10·36	9·93%	Reddish brown silky needles from alcohol. Soluble in pyridine, acetone, benzene, chloroform; sparingly soluble in alcohol and ether.
Phenylhydrazone ($C_{23}H_{24}ON_4$)		180°	...	N, 15·37	15·05	Crystallised from alcohol, the m.p. considerably depressed when mixed with the corresponding aldehyde.
Benzeneazocarvacrol aldehyde ($C_{17}H_{18}O_2N_2$)	Benzene-azocarvacrol and from diazobenzene chloride and carvacrol aldehyde (preparation of carvacrol-aldehyde described later).	135°	Light yellow	N, 10·39	9·93	Stout needles from alcohol. Soluble in chloroform, benzene, pyridine, acetone; sparingly soluble in alcohol and ether.
Phenylhydrazone ($C_{23}H_{24}ON_4$)		225°		N, 15·39	15·05	Crystallised from dilute acetic acid.

TABLE II—(contd.)

Compound.	Prepared from.	M.p.	Shade on silk.	Analysis. Found.	Calc.	Remarks.
p-Nitrobenzeneazosalicylaldehyde ($C_{13}H_9O_4N_3$)		192°-93°	Orange yellow			Reddish brown needles from toluene Identical with the compound prepared by Hewitt and Mitchel (*J. Chem. Soc.*, 1907, **91**, 1262); phenylhydrazone melts at 235°-240°.
m-Nitrobenzeneazosalicylaldehyde ($C_{13}H_9O_4N_3$)	*m*-Nitrobezeneazophenol and from diazotised-*m*-nitroaniline and salicylaldehyde	163°	Yellow	N, 15·55	15·50%	Red needles from alcohol, Highly soluble in chloroform, alcohol, acetone, pyridine; sparingly soluble in CCl_4, petroleum ether.
Semicarbazone ($C_{14}H_{12}O_4N_6$)	...	248°	...	N, 26·07	25·61	Crystallised from alcohol.
o-Nitrobenzene-azosalicylaldehyde	*o*-Nitrobenzeneazophenol	141°	Yellow	...	...	Red needles from alcohol. Identical with the compound obtained by Grandmogin and Freiman (*J. pr. Chem.*, 1908, *ii*, **78**, 384); phenylhydrazone melts at 192°.
p-Chlorobenzeneazosalicylaldehyde ($C_{13}H_9O_2N_2Cl$)	*p*-Chlorobenzeneazophenol also from *p*-chlorodiazobenzene chloride and salicylaldehyde	198°	Yellow	N, 11·54	10·75	Yellow plates from alcohol. Highly soluble in chloroform, pyridine, acetone, benzene, sparingly soluble in CCl_4.
Semicarbazone ($C_{14}H_{12}O_2N_5Cl$)	...	Does not melt below 360°	...	...	...	Crystallised from alcohol.

TABLE II—(contd.)

Compound.	Prepared from.	M.p.	Shade on silk.	Analysis. Found.	Calc.	REMARKS.
o-Chlorobenzeneazosalicylaldehyde	o-Chlorobenzeneazophenol and from o-chlorodiazobenzene chloride and salicylaldehyde	184°	Yellow	N, 11·65	10·74%	Fern-like crystals from alcohol, highly soluble in chloroform, ether, acetone, pyridine, benzene, moderately soluble in CCl_4 and alcohol; insoluble in petroleum ether.
Semicarbazone	...	259°	...	...	...	Crystallised from alcohol.
p-Toluenazosalicylaldehyde ($C_{14}H_{12}O_2N_2$)	p-Toluenazophenol and from p-methyldiazobenzene chloride and salicylaldehyde	147°	Yellow	N, 11·13	11·60	Micro-crystalline yellow powder from alcohol, highly soluble in chloroform, benzene, alcohol, pyridine, acetone, CS_2; sparingly soluble in petroleum ether.
Semicarbazone ($C_{15}H_{15}O_2N_5$)	...	250°	Yellow	N, 23·79	23·57	Crystallised from alcohol.
o-Toluenazosalicylaldehyde.	o-Toluene-azo-phenol also from o-methyl azobenzene chloride and salicylaldehyde.	120°	Yellow	N, 11·40	11·66	Yellow needles from alcohol, highly soluble in chloroform, CCl_4, acetone, pyridine, benzene, alcohol, ether, petroleum ether, CS_2.
Semicarbazone	...	196°	...	N, 23·27	23·57	Crystallised from alcohol.

Preparation of carvacrol aldehyde.—A solution of carvacrol (15 g.) in a mixture of chloroform (16 c. c.) and alcohol (50 c. c.) was added drop by drop with constant stirring to a solution of caustic soda (20 g. in 33 c. c. of water) which was kept in a flask fitted with an upright condenser. The reaction was carried at 40° for 10 hours. The alcohol and the excess of chloroform was driven off and the solution made strongly acidic when a deep red oil separated out. The mixture was distilled in steam when the aldehyde separated as a reddish oil in the distillate which was taken up with ether and purified through the bisulphite compound in the usual way. Deep red liquid boiling at 237° ; soluble in alcohol and ether, yield 1·5 g. (Found : C, 74·0 ; H, 8·01. $C_{11}H_{14}O_2$ requires C, 74·15 ; H, 7·86 per cent). This is the *ortho*-aldehyde as it is volatile with steam and gives a violet colouration with ferric chloride. The *p*-aldehyde seems not to be formed in this case. The *semicarbazone*, prepared in the usual way, crystallises from alcohol in colourless needles, m. p. 252°. (Found : N, 18·10. $C_{12}H_{17}O_2N_3$ requires N, 17·86 per cent).

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On Ketimine-enamine Compounds.

BY UMAPRASANNA BASU.

In the literature differences of opinion with regard to the mode of behaviour of ketimine-enamine tautomeric compounds in condensation reactions are largely in evidence, where the main issue has been whether the compounds react in their ketimine form (*cf.*, Burns, *J. pr. Chem.*, 1893, *ii*, **47**, 105 ; Meyer, *Chem. Centrl.*, 1908, **II**, 591), or are active in their enamine phase (Combes and Combes, *Bull. Soc. chim.*, 1893, *iii*, **7**, 778 ; Benary, Reiter and Soenderop, *Ber.*, 1917, **50**, 83). Even phenylcarbimide, a reagent which appears to have little effect upon the different isomers when dissolved in a non-ionising solvent, reacts (*cf.* Behrend and Meyer, *Ber.*, 1900, **33**, 621) with both forms of the above tautomeric compounds. Consequently they

might be regarded as existing in both the modifications particularly in the liquid state, or in solution in a condition of dynamic equilibrium; when a more complicated problem would be involved in each type of their reactions, the mode of which will depend on the conditions of the reaction, the nature of the reagent, or both.

By applying the general principles of cationotropy (*Annual Reports*, 1927, p. 106) it may be noticed that in the dissociation of the mobile hydrogen atom from the system (I) an electromeric anion (II) is left behind, where the tautomeric electron displacements $\dot{N} = \overset{\curvearrowleft}{C} - \overset{\curvearrowleft}{C} \cdot X$, bring about a redistribution of the negative charge between the nitrogen and carbon atoms, the eliminated cation (hydrogen) having thereby two points of reassociation. Accordingly the changes involved in coming into equilibrium under a particular condition are:

$$\underset{\text{Ketimine (I)}}{\dot{N} = \dot{C} - \dot{C}H \cdot X} \rightleftharpoons \left[N = C - \overset{\ominus}{C} \cdot X \right] H^{\oplus}$$

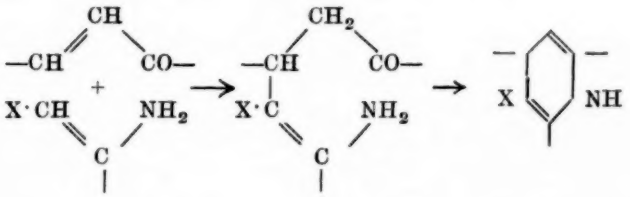
$$\underset{\text{Enamine (IV)}}{H\dot{N} - \dot{C} = \dot{C} \cdot X} \rightleftharpoons \left[\overset{\ominus}{N} - C = C \cdot X \right] H^{\oplus}$$

(II) (III)

The equilibrium of the system will consequently depend jointly on the relative stability of the two anions (II) and (III), and on that of the covalent linkages by means of which the common cation (hydrogen) associates with each of them.

Now the more electronegative nitrogen atom would have a more powerful attraction for the cation and the consequence would be that the compound would exist mainly in the enamine form (IV) in its equilibrium. Certain physical methods, such as magnetic rotation (Perkin, *J. Chem. Soc.*, 1892, **61**, 828) and absorption spectra (Auwers and Susemihl, *Ber.*, 1930, **63**, 1072), that have been so far employed to elucidiate the constitution of such compounds, favour the enamine form (IV). On the basis of this assumption the mode of various reactions of the tautomeric compounds of the ketimine-enamine type may be easily considered and an attempt may be made to find out a solution of the problems involved, although the inherent defect of the chemical method of handling equilibrium mixtures cannot but be recognised.

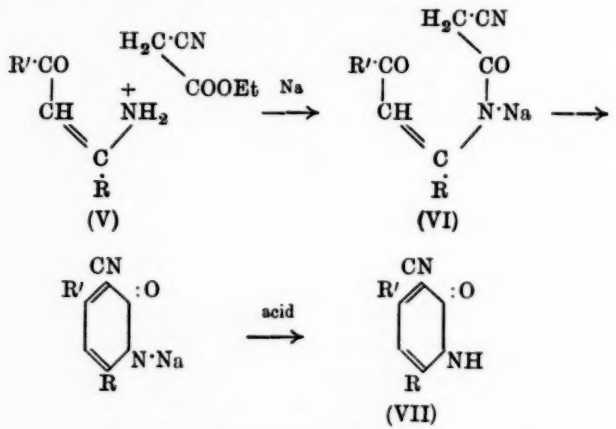
The enhanced activity of the enamine phase was first of all recorded by Beyer (*Ber.*, 1891, **24**, 1662; *cf.* also Knoevenagel, *ibid.*, 1903, **36**, 1280, 2188) who represented the reaction of ketimine-enamine compounds with $\alpha\beta$-unsaturated ketones in the following way:



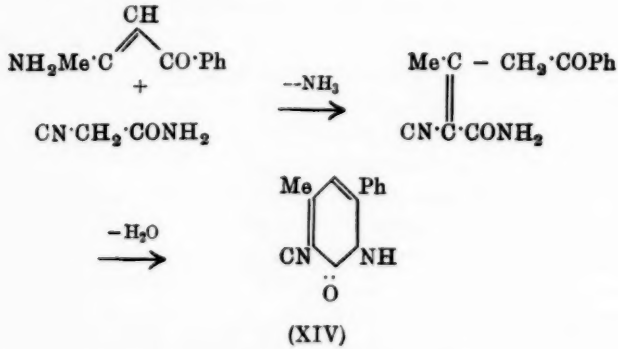
These condensations are carried out in solution or better by heating the mixture above their fusion point, either condition would favour the enamine phase (*cf.* Auwers and Susemihl, *loc. cit.*). That the enamine form is responsible for this type of condensation is also evident from two negative results previously recorded (Basu, *J. Indian Chem. Soc.*, 1931, **8**, 321) during the condensation of benzal benzoylacetone with ethyl tetrahydroanthranilate and methyl acetylacetonamine. In their reaction with hydroxymethylene ketones (Basu, *Annalen*, 1934, **514**, 292) too, it is most natural to expect that the ketimine-enamine tautomeric compounds will react in their enamine form with unsaturated ketone, HO · CH : CH · COR, represented by the hydroxymethylene phase of the dicarbonyl compound. That the acetate of hydroxymethylene *cyclo*hexanone behaves analogously (Basu, *Annalen*, 1934, **512**, 133) further supports the above hypothesis.

When the compounds are treated with esters in presence of sodium, the products of reaction are always *N*-derivatives (Benary and Schmidt, *Ber.*, 1921, **54**, 2161). In these cases the electro-negative nitrogen would attract the more positive cation sodium and the consequence would be a predominance of the enamine form (IV) in the system. Under these circumstances the ester molecule might be drawn towards the unsaturated nitrogen atom whose unsaturation has further been enormously increased by its association with the highly positive sodium atom, and the result of the reaction would be the production of *N*-acyl derivatives. A direct deduction from this idea would be a synthesis of a pyridone derivative (VII) by reacting a tautomeric compound of the type (V) with an ester molecule containing an appropriately situated methylene group, such as in ethyl cyanoacetate. The *N*-acyl derivative (VI), that would be initially

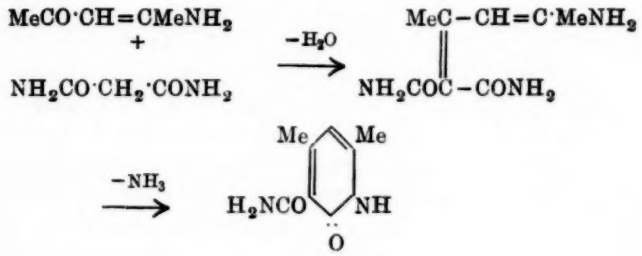
formed, might readily pass into the pyridone derivative (VII) owing to a tendency for the formation of a six-membered ring thus:



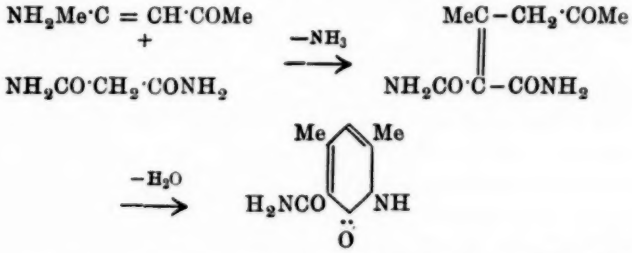
The isolation of 3-cyano-4-phenyl-6-methyl-2-pyridone (XV) from the condensation of benzoyl acetonamine with ethyl cyanoacetate in presence of sodium is quite in agreement with the above view. Quite a different problem is most likely involved in their reaction with cyanoacetamide, for the above amine gave with cyanoacetamide the isomeric pyridone derivative, 3-cyano-4-methyl-6-phenyl-2-pyridone (XIV) (Basu, *loc. cit*), the mechanism of this latter reaction being represented by the scheme:



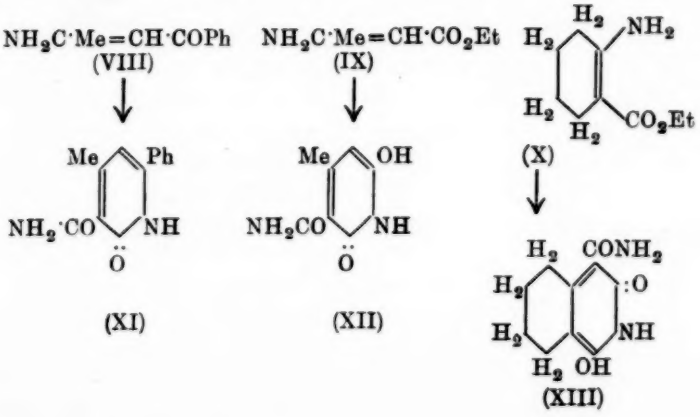
Knoevenagel and Cremer (*Ber.*, 1902, **35**, 2395), however, represented a similar action between acetyl acetoamine and malonamide in a different way thus:



But as the amine has been obtained from a symmetrical β diketone, their reaction is quite as readily explained by the mechanism:

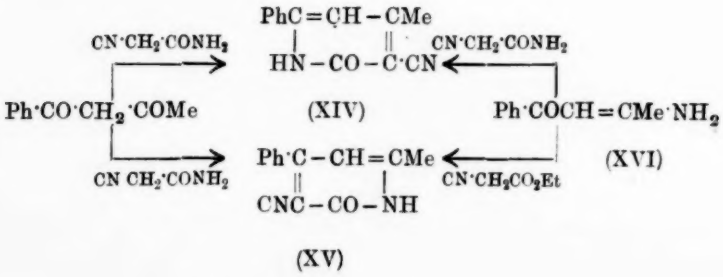


To have a clear idea on this point, three amines (VIII), (IX) and (X) have been respectively prepared from the unsymmetrical dicarbonyl compounds, benzoylacetone, ethyl acetoacetate and ethyl *cyclo*hexanone-2-carboxylate, and digested with malonamide in an oil-bath when the expected condensation products (XI), (XII) and (XIII) were isolated from the corresponding reaction mixture.



Lastly the activity of the tautomeric compounds in their ketimine form in certain cases (in the reaction of diacetonitrile with hydroxylamine hydrochloride as observed by Burns, *J. pr. Chem.*, 1893, *ii*, **47**, 105) might be due to the driving back by hydrion (the presence of hydrochloric acid increasing the concentration of hydrion), of the dissociation of the mobile hydrogen of the tautomeric compound in question, with resulting increase in the proportion of the ketimine form (1).

An interesting fact that arises out of this investigation is the directive influence of the carbethoxy group in ethyl cyanoacetate in its reaction with enamine compounds. When, however, instead of the ester cyanoacetamide is made to react with them, the directive influence disappears and the structural reactivity of the conjugated double bonded system as present in the enamine form (IV) of the tautomeric system reasserts itself. An outcome of this work, therefore, is that it provides a method of isolating and distinguishing the different isomers usually obtained in the condensation of 1:3-dicarbonyl compounds either with cyanoacetic ester in presence of ammonia according to Issoglio (*Atti. R. Accad, Sci. Torino*, 1905, **40**, 495), or with cyanoacetamide in presence of a basic condensing agent according to Sen-Gupta (*J. Chem. Soc.*, 1915, **107**, 1347). For example, benzoylacetone gives with cyanoacetamide a mixture of two pyridone derivatives (XIV) and (XV), the isolation of the latter in its pure form being extremely difficult (*cf.* Basu, *J. Indian Chem. Soc.*, 1930, **7**, 489); the amido derivative (XVI), on the contrary, gives with cyanoacetamide only the compound (XIV). The other isomer (XV), however, may be obtained by condensing the amido compound with ethyl cyanoacetate in presence of sodium.



(XV)

Experimental

Benzoylacetoneamine, (VIII) was prepared by the method of Knoevenagel (*Ber.*, 1903, **36**, 2188) and obtained in shining plates, m.p. 143°.

(*i*) *Action with malonamide.*—An equimolecular mixture of malonamide and benzoylacetoneamine was heated in an oil-bath at 175-80° for about an hour, when the reaction took place with copious evolution of ammonia. The residue was crystallised from dilute alcohol, m.p. 286-87°. (Found: N, 12·43. $C_{13}H_{12}O_2N_2$ requires N, 12·28 per cent). The compound is soluble in water, alkali and concentrated acids. On heating with 80% sulphuric acid for about half an hour it gave a product, m.p. 182° after crystallisation from alcohol. (Found: N, 7·63. $C_{12}H_{11}ON$ requires N, 7·57 per cent). The hydrolysed product is easily soluble in dilute alkali and gives a reddish colouration with alcoholic ferric chloride. It was identified as 4-methyl-6-phenyl-2-pyridone (Bardhan, *J. Chem. Soc.*, 1929, 2223); accordingly the mother compound would be 4-methyl-6-phenyl-2-pyridone-3-carbonamide (XI).

(*ii*) *Action with ethyl cyanoacetate.*—To an alcoholic solution of sodium ethoxide containing 0·9 g. of sodium, benzoylacetoneamine (6·5 g.) and ethyl cyanoacetate (4·5 g.) also dissolved in absolute alcohol was added and the mixture was heated under reflux at 110° for about 3 hours. Within half an hour a clear solution was obtained and gradually a solid separated out. After allowing the mixture to remain at the room temperature for 24 hours, water was added to have a clear solution and this on acidification gave a white solid which on crystallisation from alcohol melted at 277°. (Found: N, 13·40. $C_{13}H_{13}ON_2$ requires N, 13·33 per cent). The substance is soluble in alkali and concentrated acids from which solutions it is precipitated unchanged on acidification and dilution respectively. On hydrolysis with 80% sulphuric acid the compound gave the known 4-phenyl-6-methyl-2-pyridone, m.p. 207°, the m.p. being not depressed when mixed with an authentic sample of the pyridone obtained from the stock. Evidently the mother product was 3-cyano-4-phenyl-6-methyl-2-pyridone (XV).

(*iii*) *Action with cyanoacetmethylamide.*—An equimolecular mixture of the amine and cyanoacetmethylamide (Basu, *J. Indian Chem. Soc.*, 1930, 7, 492) when heated at 150° in an oil-bath for more than half an hour gave a product melting indifferently at

252°. It was partly soluble in caustic alkali. The main and insoluble portion separated from alcohol in prismatic needles. m.p. 266° and was found to be 3-cyano-1:4-dimethyl-6-phenyl-2-pyridone (XIV, NH=N·Me) (Basu, *J. Indian Chem. Soc.*, 1931, **8**, 327). (Found: N, 12·67. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent). The above alkaline solution on acidification gave a small quantity of 3-cyano-4-methyl-6-phenyl-2-pyridone (Issoglio, *loc. cit.*), m.p. 310°, on crystallisation from acetic acid. The isolation of the latter compound indicates that most probably the ammonia set free during the condensation reaction transforms part of cyanoacetmethylamide to cyanoactamide and it is this latter reagent that is responsible for the production of 3-cyano-4-methyl-6-phenyl-2-pyridone (XIV).

Ethyl β-aminocrotonate, Me $C(NH_2)$:CH·COOEt (IX).

(*i*) *Action with malonamide.*—The condensation was effected as usual by heating an equimolecular mixture of ethyl β-aminocrotonate (Michaelis, *Annalen*, 1909, **366**, 337) and malonamide in an oil-bath for more than an hour. The reacted mixture was then acidified with the dilute hydrochloric acid and the solid separated on crystallisation from the boiling water melted at 198° with decomposition. (Found: C, 49·89; H, 4·85; N, 16·52. $C_7H_8O_3N_2$ requires C, 50·0; H, 4·76; N, 16·66 per cent).

It dissolves in sodium carbonate solution with effervescence, is coloured bluish green when warmed with sodium nitrite solution and imparts a reddish violet colouration to an alcoholic ferric chloride solution. On boiling with caustic alkali it evolves ammonia but on heating with fuming hydrochloric acid at 150° for more than 3 hours and on subsequent neutralisation with sodium carbonate, the product yielded a different compound which on crystallisation from water melted at 194°. (Found: N, 11·12. $C_6H_7O_2N$ requires N, 11·20 per cent).

This compound is the known 4-methyl-2:6-dioxypyridine and has been previously synthesised by Rogerson and Thorpe (*J. Chem. Soc.*, 1905, **87** 1685), consequently the condensation product would be 4-methyl-6-oxy-2-pyridone-3-carbonamide (XII). This condensation was also brought about by dissolving malonamide (1 mol.) and the aminocrotonate (1 mol.) in dilute alcohol with the addition of a few c.c. of piperidine. The solution was left at the room temperature. After 4 days it was concentrated and acidified when the above carbonamide derivative separated out.

Ethyl tetrahydroanthranilate (X).—The anthranilate derivative was prepared by passing ammonia to ethyl *cyclo*hexanone-2-carboxylate according to Dieckmann (*Annalen*, 1901, **317**, 27) and was obtained in shining plates, m.p. 74°. Ethyl tetrahydroanthranilate (8·45 g.) and malonamide (5·1 g.) were intimately mixed and the mixture was heated on an oil-bath at 190° for several hours. The mass was then treated with dilute hydrochloric acid when a very small quantity of a solid was isolated. On crystallisation from dilute acetic acid it melted at 183-84°. (Found: N, 13·70. $C_{10}H_{12}O_3N_2$ requires N, 13·46 per cent).

The compound readily dissolves in sodium bicarbonate solution with effervescence, imparts a bluish violet colouration to alcoholic ferric chloride and gives a deep yellow colour with sodium nitrite solution. On hydrolysis with fuming hydrochloric acid as usual it gave a product which on crystallisation from alcohol melted at 205° and was found to be identical with 1:3-dioxy-5:6:7:8-tetrahydro*iso*quinoline (Basu, *loc. cit.*) The initial condensation product necessarily is 1-oxy-3-keto-2:3:5:6:7:8-hexahydro*iso*quinoline-4-carbonamide (XIII). A better yield of the condensation product was obtained by condensing ethyl *cyclo*hexanone-2-carboxylate with malonamide (1:1) in dilute alcoholic solution in presence of piperidine.

Benzoylacetone methylamine Me C(NH Me) : CH·CO·Ph.—This methylamine derivative was obtained by treating benzoylacetone with 33 % solution of methylamine according to Beyer (*Ber.*, 1891, **24**, 1669).

(*i*) *Action with ethyl cyanoacetate.*—An alcoholic solution of benzoylacetone methylamine (7·0 g.) was added to a solution of sodium ethoxide containing about 0·9 g. of sodium. To this ethyl cyanoacetate (4·5 g.) was then added and the mixture was heated under reflux at 110° for more than 5 hours. On careful acidification and dilution with water the mixture gave unchanged benzoylacetone methylamine indicating thereby that no reaction had taken place in this case as there was no chance for the formation of an intermediate sodium salt of the type (VI).

(*ii*) *Action with cyanoacetamide.*—An intimate mixture of the methyl amide and cyanoacetamide in molecular quantities was heated together in an oil-bath at 125° for about half an hour, when the usual reaction took place with copious evolution of ammoniacal vapour. The major portion of the condensation product was found to be soluble in alkali and from the alkaline solution a compound was isolated

which on recrystallisation from glacial acetic acid melted at 310°. This was found to be 3-cyano-4-methyl-6-phenyl-2-pyridone already referred to. (Found: N, 13·33. $C_{13}H_{10}N_2$ requires N, 13·33 per cent).

The insoluble product was crystallised from alcohol when it melted at 266°, the m. p. being not depressed when admixed with the compound 3-cyano-1:4-dimethyl-6-phenyl-2-pyridone previously obtained by reacting benzoylacetoneamine with cyanoacetmethylamide.

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Dimercaptothiobiazole as an Analytical Reagent.

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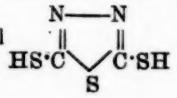
In a note published previously (*J. Indian Chem. Soc.*, 1934, **11**, 403) by one of us (J.G.) reference was made to the use of dimercaptothiobiazole or thiobiazole-1:4-dithiol  as a very convenient reagent for the estimation of copper, lead and bismuth, and for their separation from the metals of the II **B** group and the rest of the analytical groups (*e.g.*, As, Sb, Sn, Mo, Fe, Zn, etc.). Mention was also made of its usefulness as a qualitative micro-reagent for Cu and Bi.

The substance behaves as a weak acid like H_2S, the hydrogen atoms of the sulphydryl groups being replaceable by metals under suitable conditions. It gives characteristic coloured precipitates with most of the elements of the H_2S-group of the analytical table. The precipitates obtained in most of these cases were, however, of variable composition and could not, therefore, be directly weighed, but they settled readily and were easily separated by filtration.

EXPERIMENTAL.

Preparation of the reagent.—Thiobiazole-1:4-dithiol was most conveniently prepared according to the methods described by

Losanitsch (*J. Chem. Soc.*, 1922, **121**, 2544) from carbon disulphide and hydrazine hydrate in alcoholic ammonia and was purified by recrystallisation from ether, m.p. (Losanitsch), 168°; m.p. (found), 168-69°. A solution of the ammonium salt of the reagent was used in the estimations.

The substance is slightly soluble in cold water, more in hot, but easily soluble in dilute ammonia and alcohol An aqueous solution of the reagent behaves with some of the soluble metallic salts in the following way:

TABLE I.

Salts of.	Behaviour.
Copper	Insoluble brown precipitate, turns granular in presence of mineral acids.
Cadmium	Yellowish white crystalline precipitate, soluble in acids.
Lead	Bright yellow granular precipitate, insoluble in very dilute nitric acid and in organic acids like acetic and tartaric.
Bismuth	Bright red precipitate, insoluble in very dilute nitric acid and in organic acids, but soluble in dilute HCl.
Silver	Dirty white granular precipitate, insoluble in very dilute nitric acid.
Mercury	Yellow precipitate, insoluble in nitric acid.
Arsenic Antimony Tin (stannous)	Yellow precipitate, partly soluble on heating.
Zinc	Sparingly soluble white precipitate, readily soluble in mineral acids.
Thorium	Yellow crystalline precipitate, soluble in excess of the reagent (*cf.* Losanitsch, *loc. cit.*).

Detection and Estimation of Copper.

For sensitiveness and identification limits, a dilute hydrochloric acid solution of the salt and an aqueous solution of the reagent were used. The salt used was copper sulphate.

Precipitation limit = 1 part in 1,600,000 parts.

Colouration limit = 1 part in 6,500,000 parts.

Identification limit = 0·02 μg.

(*One μg is one millionth part of a gram* = 1 *microgram* = γ).

As the composition of the copper precipitate was variable, the metal was estimated volumetrically by decomposing the moist precipitate with nitric acid (1:1 by volume). The solution was filtered from any undissolved sulphur, and evaporated to a small bulk (5 c.c.), after the addition of a little bromine water, to remove all nitrous acid and most of the nitric acid. Copper was then estimated iodometrically in the usual way.

Separation of Copper from Iron.

A solution of copper sulphate (Kahlbaum, "Pro Analysi") of approximately 1 % Cu was prepared and the copper content was determined by the Quinaldinate method (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400). A solution of ferric chloride of about the same strength was also prepared from the chemically pure salt, and its iron content was determined by analysis.

A mixture of the known volumes of the two solutions was warmed with sulphurous acid to reduce the iron to the ferrous state and thus to avoid an undesirable precipitation of the condensation product of the reagent, as ferric chloride oxidises the dithiol to disulphide. The solution was diluted to a volume of 180-200 c.c., acidified with 5-15 c.c. of $2N$-H_2SO_4 (more acid is not harmful), heated to boiling; and to this the reagent (solution of the ammonium salt of the dithiol) was added, drop by drop, with constant stirring. After allowing the precipitate to settle, the solution was filtered hot, washed several times by decantation with hot water, finally transferred and washed free from sulphate. The moist precipitate was then transferred to the same beaker in which it was contained, decomposed with nitric acid (1:1) and estimated iodometrically with $N/20$-$Na_2S_2O_3$. Iron was estimated in the filtrate by decomposing the reagent with a little bromine water, boiling off the excess of bromine and precipitating the metal as hydroxide. The results are given in Table II.

TABLE II.

	Metals present.	Metals found.	Error.
1.	Cu, 0·0528 g. Fe, 0·1192	Cu, 0·0530 g. Fe, 0·1193	+0·0002 +0·0001
2.	Cu, 0·0528 Fe, 0·0596	Cu, 0·0528 ...	Nil ...
3.	Cu, 0·0528 Fe, 0·1192	Cu, 0·0530 ...	+0·0002 ...
4.	Cu, 0·0211 Fe, 0·1192	Cu, 0·0212 Fe, 0·1192	+0·0001 Nil
5.	Cu, 0·0845 Fe, 0·0596	Cu, 0·0845 Fe, 0·0596	,, ,,
6.	Cu, 0·0792 Fe, 0·0358	Cu, 0·0792 Fe, 0·0358	,, ,,
7.	Cu, 0·0211 Fe, 0·1192	Cu, 0·0212 Fe, 0·1193	+0·0001 +0·0001
8.	Cu, 0·0106 Fe, 0·2384	Cu, 0·0106 ...	Nil ...

Separation of Copper from Zinc.

The zinc solution was prepared by dissolving chemically pure zinc sulphate in water containing a little free sulphuric acid. The strength of the solution was determined by estimating zinc as zinc ammonium phosphate.

A mixture of the known volumes of copper and zinc solutions was diluted to 180-200 c.c. and acidified with 5 c.c. of 1:4 (by volume) sulphuric acid. The solution was heated to boiling and the copper precipitated as before. The precipitate was first washed with hot water containing a little dilute sulphuric acid, and then with hot water alone. Copper was estimated from the moist precipitate as described previously. The filtrate was treated with bromine water to decompose the reagent, concentrated to about 350 c.c., and the zinc precipitated and estimated as zinc ammonium phosphate. The results are tabulated below:

TABLE III.

Metals present.	Metals found.	Error.
1. Cu, 0·0528 g.	Cu, 0·0528 g.	Nil
Zn, 0·0976	Zn, 0·0977	+0·0001
2. Cu, 0·0739	Cu, 0·0740	+0·0001
Zn, 0·0488	Zn, 0·0488	Nil
3. Cu, 0·0317	Cu, 0.0317	Nil
Zn, 0·0976	Zn, 0·0976	Nil
4. Cu, 0·1056	Cu, 0·1055	−0·0001
Zn, 0·0195	Zn, 0·0195	Nil
5. Cu, 0·0739	Cu, 0·0740	+0·0001
Zn, 0·0683	Zn, 0·0683	Nil

Separation of Copper from Arsenic (tri-and pentavalent).

Separation was effected in the presence of ammonium fluoride to prevent any precipitation of arsenic by the reagent. The copper and arsenic solutions were mixed, and fifteen times the weight of ammonium fluoride, as there was arsenic present, were added. The solution was diluted to about 180 c.c., acidified with 5 c.c. of $2N$-H_2SO_4 (more acid is not harmful), and the copper was precipitated as usual. The precipitate was twice decanted with hot water containing at first a small quantity of ammonium fluoride, then with hot water alone. The precipitate was dissolved in nitric acid and treated as usual.

TABLE IV.

Cu present.	As added.	Cu found.	Error.
1. 0·0528 g.	0·05 g.	0·0528 g.	Nil
2. 0·0739	0·015	0·0736	−0·0003
3. 0·0211	0·10	0·0211	Nil

The estimation of arsenic in the filtrate was deemed unnecessary as a check, as its presence in the copper precipitate would vitiate the titration value.

Separation of Copper from Antimony (tri-and pentavalent).

As in the case of arsenic, the separation was effected in the presence of ammonium fluoride which forms a complex ion with antimony preventing its precipitation by the reagent.

The amount of fluoride added was approximately fifteen times the weight of antimony present. The volume of the solution was diluted to about 180 c.c. and the copper was precipitated in the usual way. The washing and further treatment of the precipitate was exactly similar to those employed in the case of arsenic-copper separation.

TABLE V.

Sb added.	Cu present.	Cu found.	Error.
1. 0·06 g.	0·0528 g.	0·0529 g.	+0·0001
2. 0·02	0·0739	0·0739	Nil
3. 0·11	0·0211	0·0211	Nil

The antimony in the filtrate can be estimated after decomposing the fluoride by heating with boric acid.

Separation of Copper from Tin (stannic).

The separation of copper from stannic tin is rendered easier by the fact that tartaric acid prevents the precipitation of tin by the reagent.

A solution of stannic tin was prepared by dissolving chemically pure tin in potassium chlorate and hydrochloric acid. The strength of the solution was determined by estimating the tin as dioxide.

Known volumes of copper and tin solutions were mixed. 4-5 G. of solid tartaric acid were added to the mixture and the solution diluted to 150—200 c.c. This was rendered strongly acidic with

1 c.c. of concentrated HCl, and the copper precipitated and estimated in the usual way,

Tin in the filtrate was estimated by precipitating with H_2S in hot solution, washing and igniting the sulphide to dioxide, at first very carefully, and finally over the blast-lamp.

TABLE VI

Metals present.	Metals found.	Error.
1. Cu, 0·0528 g. Sn, 0 12 5	Cu, 0·0527 g. —	−0·0001 —
2. Cu, 0·0317 Sn, 0·0632	Cu, 0·0317 Sn, 0·0629	Nil −0·0003
3. Cu, 0·0211 Sn, 0·1265	Cu, 0·0211 Sn, 0·1271	Nil +0·0006
4. Cu, 0·0528 Sn, 0·1265	Cu, 0·0530 —	+0·0002 —
5. Cu, 0·0422 Sn, 0·0759	Cu, 0·0422 —	Nil —
6. Cu, 0.0211 Sn, 0·0632	Cu, 0·0211 Sn, 0·0632	Nil Nil
7. Cu, 0·0739 Sn, 0·0379	Cu, 0·0743 Sn, 0·0382	+0·0004 +0·0003
8. Cu, 0·0528 Sn, 0·0632	Cu, 0·0528 —	Nil —

The estimation of tin as oxide by igniting the sulphide is known to give invariably high results. The separation of stannous tin is also easily effected in the presence of ammonium fluoride, as described under antimony.

Separation of copper from molybdenum was easily effected as the reagent does not give any precipitate with molybdenum in acid solutions. The total volume of the solution varied from 160—200 c.c. and was acidified with 5—10 c.c. of $2N$-H_2SO_4. A large excess of the reagent should be avoided, as this causes reduction of molybdenum, which is difficult to wash away completely from the precipitate. The method of procedure was similar to those already described, only that the reagent solution should be more dilute. The precipitate was first washed with hot water containing a little sulphuric acid, and finally with hot water alone.

TABLE VII.

	Mo added.	Cu present.	Cu found.	Error.
1.	0·05 g.	0·0528 g.	0·0528 g.	Nil.
2.	0·01	0·0739	0·0739	,,
3.	0·10	0·0211	0·0211	,,

Separation of copper from tungsten.—Tungsten gives no precipitate with the reagent in acid solutions, but there is a tendency for the tungstic acid itself to separate out. On the other hand, the precipitate of copper obtained in neutral solutions is not easily filtrable. Hence a solution, rather dilute with respect to tungstic acid, was employed. Of the mineral acids, sulphuric acid was found to hold tungstic acid fairly well in solution. The volume of the solution was made up to 160—270 c.c. and acidified with 5 c.c. of $2N$-H_4SO_4. The precipitate was first washed twice with hot water containing a little dilute sulphuric acid, and finally with hot water alone. The copper was estimated as usual.

TABLE VIII.

	W added.	Cu present.	Cu found.	Error.
1.	0·05 g.	0·0528 g.	0·0527 g.	−0·0001
2.	0·02	0·0739	0·0739	Nil

Solutions, more concentrated with respect to tungstic acid, cause precipitation of the latter.

Estimation of lead.—Lead was precipitated from a solution containing tartaric or acetic acid in the form of a dense bright yellow precipitate, easily filtrable. The precipitate was washed, dried partially for 10—15 minutes in an air-oven, and most of it was transferred and kept on a covered watch-glass. The filter-paper was gently heated in an open crucible over a low flame till the paper was completely consumed. The whole of the precipitate was then transferred into the crucible, treated with concentrated HNO_3 on the water-bath, covering the crucible with a watch-glass. After the decomposition of the precipitate and evaporation of most of the nitric acid, the residue was carefully evaporated with sulphuric acid. The last traces of the acid were removed by heating the crucible in a larger crucible, and the lead sulphate weighed.

Separation of lead from tin (stannic).—Extra pure lead acetate was dissolved in water containing free acetic acid. The strength of the solution was determined by evaporating a known volume of the solution to dryness with dilute sulphuric acid. Known volumes of lead and tin solutions of definite strength were mixed. Ammonium tartrate (3—5 g.) was added and the solution diluted. This was then rendered alkaline with ammonia when any precipitate previously formed dissolved completely. The solution was afterwards made slightly acidic

to litmus by the addition of acetic or tartaric acid. Excess of the latter should be carefully avoided as it precipitates the acid tartrate. The solution was then diluted to 150 c.c., heated to boiling, and the lead was precipitated by the gradual addition of the reagent (solution of the ammonium salt of the dithiol) with stirring. The precipitate was allowed to settle for 5 minutes, washed twice by decantation with hot water containing a little tartaric acid, and finally with hot water alone. The precipitate was then further treated as described above.

TABLE IX.

	Sn present.	Pb present.	Pb found.	Error.
1.	0·05 g.	0·0431 g.	0·0431 g.	Nil
2.	0·10	0·0172	0·0172	,,
3.	0·015	0·0603	0·0601	−0·0002

Separation of lead from antimony (tri- and pentavalent) was effected in the presence of fluoride. To the mixed solution of lead and antimony, ammonium tartrate (3—5 g.) was added to prevent the precipitation of lead fluoride, and the solution then made slightly ammoniacal. This was diluted to 200 c.c., and fifteen times the weight of ammonium fluoride, as there was antimony present, were added. The solution was then rendered slightly acidic with tartaric or acetic acid, and the lead precipitated from the hot solution as usual. The precipitate after standing for five minutes was filtered, washed first with hot water containing a little fluoride, then with hot water alone. It was dried and estimated in the usual way.

TABLE X.

	Sb present.	Pb present.	Pb found.	Error.
1.	0·05 g.	0·0431 g.	0·0433 g.	+0·0002
2.	0·10	0·0172	0·0173	+0·0001
3.	0·015	0·0603	0·0605	+0·0002

The slightly high results are evidently due to the action of fluorides on the glass beaker, this can be prevented by using normal sodium fluoride.

Separation of Lead from Molybdenum and Alkaline Earths.

From molybdenum.—To the mixed solution of lead and molybdenum, ammonium tartrate (3—5 g.) added, and the solution rendered feebly acidic to litmus, It was diluted to about 200 c c. and the lead precipitated from the hot solution as usual, avoiding an unnecessary excess of the reagent. The precipitate was treated as usual and weighed as lead sulphate.

From the alkaline earths.—This separation was effected in acetic acid solution. The mixed solution was diluted to about 180 c.c., glacial acetic acid (2—10 c.c.) added, and as usual lead was precipitated and weighed as lead sulphate.

TABLE XI.

	Metals present.	Pb present.	Pb found.	Error.
1.	Mo, 0·05 g.	0·0431 g.	0·0431 g.	Nil
2.	0·015	0·0603	0·0603	,,
3.	0·10	0·0172	0·0172	,,
4.	Ca, Sr, Ba 0·20	0·0431	0·0431	,,

Detection and Separation of Bismuth.

On account of the bright red colour of the precipitate, bismuth can be detected by means of the reagent in presence of all other elements except copper. The only other possible interfering elements are lead, arsenic, antimony, tin and mercury which give coloured precipitates. The precipitation of arsenic, antimony and tin, if present, was prevented by the addition of alkali fluoride. The detection in presence of mercury and lead was carried out by adding a dilute solution of the reagent, drop by drop, to a dilute nitric acid solution of the metals.

The test is extremely sensitive. A very dilute nitric acid solution of bismuth and an aqueous solution of the dithiol were used:

Precipitation limit = 1 part in 200,000 parts.
Colouration limit = 1 part in 1,600,000 parts.
Identification limit = 0·1 μg.

Dübsky and Okac (*Z. anal. Chem.*, 1934, **96**, 267) obtained the following values in hydrochloric acid solution of bismuth:

Sensitivity = 1 part in 28,000 parts.
Identification limit = 0·0012 mg. or 1·2 μg.

These values confirm the observation that the bismuth precipitate has a slight solubility in hydrochloric acid.

In acid solution the bismuth precipitate does not give any constant composition—a fact confirmed by Dübsky and Okac (*loc. cit.*). They, however, claim to have obtained a substance of definite composition, having the chemical formula $Bi(C_2HN_2S_3)_3$, by precipitating a faintly acid solution of bismuth nitrate with the reagent, neutralised with two molar proportions of KOH.

Bismuth has been found to be completely precipitated from solutions containing even excess of tartaric acid or ammonium fluoride. The solutions should not contain free mineral acids, but should be acidified with weak acids like acetic or tartaric. This affords a quantitative separation of bismuth from arsenic, antimony, tin and molybdenum.

Summary.

1. Some insoluble salts of dimercaptothiobiazole have deen described.

2. The precipitation, colouration and identification limits of Cu- and Bi-compounds have been determined.

3. Copper has been separated from As, Sb, Sn, Mo, W, Fe, Zn and all metals of group III (analytical) and succeeding groups.

4. Lead has been separated from As, Sb, Sn, Mo and alkaline earths in presence of tartaric acid and alkali fluoride.

5. The utility of dimercaptothiobiazole as a qualitative microreagent for Bi has been stressed, and the possibility of separating the latter quantitatively from As, Sb, Sn and Mo has been indicated.

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The Alkylation of Acetoacetic Ester by Toluenesulphonic Esters.

By C. Narayanan Nair and D. H. Peacock.

Lapworth and Ferns (*J. Chem. Soc.*, 1912, **101**, 273) prepared a number of tolueuesulphonic esters and used them in the preparation of ethers and amines. It was later found that toluenesulphonic ester could be used in the alkylation of malonic ester (Peacock and Tha, *J. Chem. Soc.*, 1928, **131**, 2303) and the process has been applied by Slotta and Franke (*Ber.*, 1930, **63**, 682), Clemo and Tenniswood (*J. Chem. Soc.*, 1931, 2550), and Tabern and Volwiler (*J. Amer. Chem. Soc.*, 1934, **56**, 1139). For the purpose of another investigation a series of ketones of the type RR'CH·CO·Me was required and in the present paper it is shown that toluenesulphonic esters may be employed in the alkylation of acetoacetic ester. The toluenesulphonic esters employed were all derived from alcohols of the type $R{\cdot}O{\cdot}C_2H_4OH$, where R was an aromatic radical. These alcohols, which have previously been described by Boyd and Marle (*J. Chem. Soc.*, 1914, **105**, 2128), were prepared by the general method used by Peacock and Tha (*loc. cit.*). A number of toluenesulphonic esters are described as well as an improved method of preparation.

It was found that the rate of reaction between the ester and the sodium derivative of acetoacetic ester was accelerated by the addition of potassium iodide to the mixture; the effect was probably due to the intermediate formation of the iodide (*cf.* Peacock and Menon, *J. Indian Chem. Soc.*, 1925, **2**, 240). The toluenesulphonic ester of phenol and of β-naphthol did not react with sodioacetoacetic ester.

Experimental.

β-Phenoxyethyl-p-toluenesulphonate.—The method previously described by Peacock and Tha (*loc. cit.*) has been improved. *p*-Toluenesulphonyl chloride (100 g.) was dissolved in acetone (400 c.c.), cooled to 10° and stirred. β-Phenoxyethyl alcohol (70 g.) and caustic soda solution (20%, 100 c.c.) were added gradually during about 2 hours. The temperature of the mixture was then allowed to rise to 30° to complete the reaction and the contents of the flask poured into cold water; the crude ester (135 g., 93%) then solidified. It was crystallised from alcohol, m.p. 80°.

The toluenesulphonic esters of phenol (Reverdin and Crepieux, *Ber.*, 1902, **35**, 1439) and β-naphthol were similarly prepared.

γ-Phenoxybutyric acid.—Sodium (2·3 g.) was dissolved in absolute alcohol (90 c.c.) and acetoacetic ester (13 g.) and β-phenoxyethyl-*p*-toluenesulphonate (29·2 g.) added. The reaction mixture was boiled under reflux for 24 hours. The sodium *p*-toluenesulphonate was then filtered off and the alcohol removed from the filtrate by distillation. The crude ester was then saponified by heating with alcoholic caustic potash (20 g. of caustic potash in 40 c.c. of aqueous alcohol) for 8 hours. Water was added and the alcohol removed by distillation. The residue was extracted with benzene to remove neutral products and then acidified. The semi-solid acid was extracted with benzene leaving a sparingly soluble residue (B) and the acid fractionally extracted from the benzene with sodium bicarboante solution. The first extracts on acidification gave γ-phenoxybutyric acid, m. p. 63° from petrol (Bentley, Haworth and Perkin, *J. Chem. Soc.*, 1896, **69**, 169, give m.p. 64-65°). [Found: Equiv (by titration) 182, (by silver salt), 182·5. $C_{10}H_{12}O_3$ requires Equiv., 180].

The later sodium bicarbonate extracts gave on acidification a substance identical with (B) above, m.p. 156-57° with evolution of carbon dioxide. It gave no colour with ferric chloride, M.W. (Rast) 210.

In the following table is shown the effect of the addition of potassium iodide to the reaction mixture. At the end of the time specified, excess of standard hydrochloric acid was added and the unused acid determined by titration with standard sodium carbonate solution. The percentage of sodium derivative used up was calculated from these figures.

Time of heating	...	1/2 hr.	1 hr.	3 hrs.
% of reaction without KI	...	22·1	36	48·4
,, ,, with KI	...	30·6	43·5	61·3

γ-Phenoxypropyl methyl ketone. (Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 651).—Acetoacetic ester (55 g.) was condensed with β-phenoxyethyl-*p*-toluenesulphonate (98 g.) in the way already described; the acetoacetic ester was in 25% excess and the reaction mixture was heated for 30 hours. The crude ester (80 g.) was saponified by heating for 16 hours with a solution of caustic potash (30 g. in rectified spirit (550 c.c.). Alcohol (200 c.c.) was then distilled off and the residue heated for a further 5 hours. The alcohol was then removed by distillation under reduced pressure using a fractionating column and the residue steam distilled. The ketone solidified (80 g., 17%). It was crystallised from petrol ether, m.p. 53-54°. [Found: C, 73·86;

H, 8·21; M.W. (in acetic acid), 165·5. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·86%. M.W., 178]. The residual aqueous solution gave γ-penoxybutyric acid (4 g.) and ββ-diphenoxyethylacetic acid (3 g.). The ketone gave *semicarbazone*, which crystallised from aqueous alcohol, m.p. 144°. (Found: N, 17·8. $C_{12}H_{17}O_2N_3$ requires N, 17·8 per cent). The *oxime* crystallised from petrol ether, m.p. 78°. (Found: N, 7·3. $C_{11}H_{15}O_2N$ requires N, 7·2 per cent).

γ-*Phenoxy-α-benzylbutyric acid*.—α-Aceto-γ-phenoxybutyrate was prepared as already described and converted without isolation to the sodium compound and condensed with benzyl chloride by further heating for 4 hours. The crude ester (68 g.) was saponified by heating for 20 hours with alcoholic caustic potash (4g. in 100 c.c. of aqueous alcohol). The crude acid obtained from the potassium salt was distilled (b.p. 250-280°/35mm., yield 17g., 32%) and solidified on keeping. It was crystallised from petrol, m.p. 77°. [Found: Equiv. (by titration), 269·1; C, 75·75; H, 7·0. $C_{17}H_{18}O_3$ requires Equiv., 270; C, 75·55; H, 6·66 per cent). The acid was converted by thionyl chloride into the acid chloride and thence to the *amide*, crystals from dilute alcohol, m.p. 125-26°. (Found: N, 5·35. $C_{17}H_{19}O_2N$ requires N, 5·2 per cent). Ketonic hydrolysis failed to give the required ketone.

β-p-*Chlorophenoxyethyl-p-toluenesulphonate*. — β-*p*-Chlorophenoxyethyl alcohol (Boyd and Marle, *J. Chem. Soc.*, 1914, **105**, 2128) was prepared by heating *p*-chlorophenol (128·5 g.), caustic soda (40 g. in 300 c.c. of water) and ethylene chlorhydrin (60 g.) under reflux on a sand-bath for 2 hours. The product was washed with caustic soda to remove the excese of *p*-chlorophenol, dried and distilled at 178°/35mm., yield 106 g.. This was converted to the toluenesulphonic ester in a way similar to that described for phenoxyethyl alcohol ; yield of crude ester, 92%. Crystallised from methylated spirit, m.p. 79°. (Found: C, 54·89; H, 4·56. $C_{15}H_{15}O_4ClS$ requires C, 55·1; H,4·59 per cent).

γ-p-*Chlophenoxybutyric acid*.—The above ester (20·4 g.) was heated for 30 hours with an absolute alcoholic solution of the sodium derivative of ethyl acetoacetate (8·13 g.) The crude ester (26 g.) was saponified by boiling with alcoholic caustic potash (7 g. in 40 c.c. of ethyl alcohol) for 11 hours. The crude acid was purified by solution in sodium bicarbonate and reprecipitation (yield 2·6g., 20%). After crystallisation from petrol ether it melted at 120°. [Found: Equiv. (by titration), 215; Cl, 16·3. $C_{10}H_{11}O_3Cl$ requires Equiv., 214·5; Cl, 16·5 per cent).

γ-p-*Chlorophenoxypropyl methyl ketone*.—The crude ketone, b.p. 170-195°/ 35 mm., was obtained from the portion insoluble in caustic potash in the above preparation. The *semicarbazone* crystallised from methylated spirit, m.p. 178°. (Found: N, 15·3. $C_{12}H_{16}O_2N_3Cl$ requires N, 15·5 per cent).

β-m-*Chlorophenoxyethyl*-p-*toluenesulphonate* was prepared in a way similar as the *p*-isomer, m.p. 57°. (Found: Cl, 10·66. $C_{15}H_{15}O_4ClS$ requires Cl. 10·68 per cent).

γ-m-*Chlorophenoxybutyric acid*.—The above ester (11 g.) was condensed with the sodium derivative of ethyl acetoacetate (5 g.) by boiling in absolute alcohol solution for 30 hours, yield of crude ester 9·2 g. This was saponified by heating with caustic potash (5 g. in 25 c.c. of aqueous alcohol) for 11 hours. The acid obtained (1·8 g.) was crystallised from petrol ether, m.p. 51-52°. [Found: Equiv. (by titration), 216; Cl, 16·23. $C_{10}H_{11}O_3Cl$ requires Equiv., 214·5; Cl, 16·57 per cent].

γ-m-*Chlorophenoxypropyl methyl ketone*.—The crude ketone from the above preparation weighed 3 g., b.p. 180-200° /35 mm. The *semicarbazone* crystallised from methylated spirit, m.p. 146°. (Found: N, 15·7. $C_{12}H_{16}O_2N_3Cl$ requires N, 15·5 per cent).

β-β-*Naphthoxyethyl*-p-*toluenesulphonate*.—The required alcohol was prepared from ethylene chlorhydrin and β-naphthol (*cf.* Boyd and Marle, *loc. cit.*) It was converted to the sulphonate as already described, yield 82%. It crystallised from methylated spirit, m.p. 90°. (Found: S, 9·03. $C_{19}H_{18}O_4S$ requires S, 9·35 per cent).

γ-β-*Napthoxybutyric acid*.—The above ester (14 g.) was boiled for 30 hours with an absolute alcoholic solution of the sodium derivative of ethyl acetoacetate (5 g.) The crude ester (15 g.) was boiled for 4 hours with a solution of caustic potash (6 g. in 30 c.c. of ethyl alcohol). The crude acid (3 g.) crystallised from dilute alcohol, m.p. 122°. [Found: Fquiv. (by titration), 231·6; C, 72·6; H, 6·10. $C_{14}H_{14}O_3$ requires Equiv., 230; C, 73·0; H, 6·00 per cent].

γ-β-*Naphthoxypropyl methyl ketone*.—The crude ketone from the above preparation weighed 3 g., b.p. 220-230° /25 mm. The *semicarbazone* crystallised from methylated spirit, m.p. 174°. (Found: N, 14·8. $C_{16}H_{19}O_2N_3$ requires N, 14·6 per cent).

We have to thank the University of Rangoon for a grant towards the expenses of this investigation.

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Investigations on the Adsorptive Property of Silica Gel. Part I. Chemical Activity of Residual Water in Activated Silica Gel.

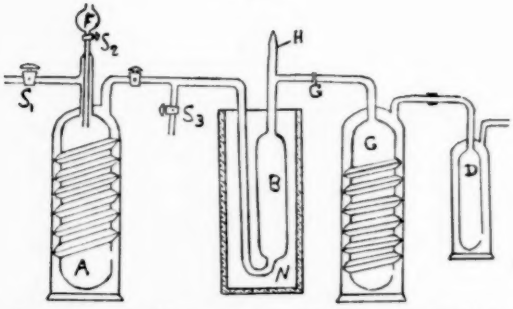
By M. R. Aswathanarayana Rao and Basrur Sanjiva Rao.

It is well known that silica gel contains some residual water which is very difficult to remove. This small quantity of strongly adsorbed water seems to have great chemical activity. In the course of an investigation (unpublished) on the reaction between hydrogen sulphide and sulphur dioxide, it was noticed that these two gases (which do not interact in the dry state) combined with great vigour at the surface of activated silica gel. The present paper gives an account of the experiments on the hydrolysis of carbon tetrachloride by the residual water in activated silica gel. The experiments indicate the great chemical activity of the adsorbed water. The investigation was the result of a violent explosion in the laboratory caused by the development of enormous pressure, in a closed glass vessel in which carbon tetrachloride had been kept in contact with silica gel at 150°.

Experimental.

The silica gel employed was a commercial product supplied by the Silica Gel Corporation. It was purified by treatment with concentrated nitric acid and activated in an electric furnace at a temperature of 353° in a stream of dry and pure air. The activated gel had a water content of 3·35% as determined by ignition to constant weight in a platinum crucible at blast lamp heat.

Fig. 1.



The carbon tetrachloride used was a C. P. product which was tested for impurities and purified by the usual methods employed in organic

chemistry. The apparatus consisted of a **U**-tube (Fig. 1) containing silica gel heated to a proper temperature by an electric furnance N. Nitrogen freed from carbon dioxide and oxygen by passing through an alkaline solution of sodium hydrosulphate and dried over phosphorus pentoxide was bubbled through a bubbler **A**, containing carbon tetrachloride and then passed over the heated gel. The products of reaction were absorbed in a known volume of standard barium hydroxide, kept in C, which was protected by D from atmospheric contamination.

A weighed amount of the gel was introduced into the **U**-tube B, through H and the open end sealed off. Stop-cocks S_1 and S_2 were closed, the apparatus attached to a Hyvac pump at the ground glass joint G. The system was evacuated for an hour and the carbon tetrachloride was poured into A, through a dropping funnel F. After allowing the gel to adsorb carbon tetrachloride for 20 minutes, the nitrogen was allowed to fill the apparatus. The apparatus was then disconnected from the pump and the bubbler system was attached to it at G. The **U**-tube was then gradually heated up to the required temperature. Nitrogen was saturated with carbon tetrachloride in A, and passed over the gel at a constant rate of one litre per hour, till the baryta freshly placed at C, remained clear, indicating that the evolution of carbon dioxide had ceased.

Preliminary experiments indicated that the barium hydroxide in C, was converted into the carbonate and the chloride by the products of reaction. The excess of baryta in C at the end of the experiment was estimated by titrating the solution with standard nitric acid ($N/10$) using phenolphthalein as an indicator and taking suitable precautions to prevent the loss of carbon dioxide. A known volume of the standard acid was then added, the solution boiled to expel carbon dioxide and the excess of the acid determined. The chloride formed could indirectly be calculated with these data, but was also directly estimated by Volhard's method. There was good agreement between chloride value obtained by the two methods.

The products of reaction were tested for free chlorine and none was found ; but the presence of carbonyl chloride in them was revealed by the following experiment. The nitrogen issuing at G, was passed through toluene saturated with ammonia, and the precipitate obtained was shaken with absolute alcohol and filtered. The alcoholic filtrate gave test for urea (*cf.* Allen, "Commercial Organic Analysis," Vol. VII, p. 293). It has to be pointed out that at a certain stage

the gel contained no water. This shows that the reaction at the gel surface is a hydrolytic process and not any thermal decomposition of carbon tetrachloride. The rate at which the hydrolysis took place is indicated by the following values obtained when 2·6 g. of the gel were heated at 300°.

TABLE I.

CO_2 (m.mole)	2·21	3·11	4·50	4·82
Time (hr.)	2	4	18	37

The gel contained 5·02 millimoles of water.

Effect of temperature on the rate of reaction.—Silica gel saturated with carbon tetrachloride and kept for three months at the laboratory temperature gave no indication of any hydrolysis. The lowest temperature at which the hydrolysis was detected was 119°. At 120° the carbon doixide evolved in one hour was 0·304 millimoles per g. of the gel. At 200° the value was 0·041 and at 300°, 0·37 millimoles per g.

Residual hydrogen chloride in the gel.—It was noticed that the hydrogen chloride produced during the reaction was not completely removed from the gel by a stream of nitrogen. For instance at the end of an experiment, the gel was found to have 9% of HCl by weight and only traces of this could be removed by passing a stream of nitrogen through S_3 for 6 hours at 300°. Details of the experiment are given below.

TABLE II.

Wt. of gel.	Temp. of gel.	Duration of expt.	HCl absorbed by baryta.
1	2	3	4
1·500 g.	200°	45 hr.	2·75 m.mol.
2·699	330	37	11·89
2·148	400	30	10·47

Residual HCl in the gel.	Residual HCl in the gel by wt.	Total HCl produced.	CO_2 absorbed by baryta.
5	6	7	8
2·61 m.mol.	6·35%	5·36 m.mol.	[1·29 m.mol.
7·47	10·22	19·36	4·97
6·07	10·33	16·54	4·08

HCl : CO_2.	Intial water in the gel.	Residual water in the gel as calc. from CO_2.	Remarks.
9	10	11	12
4·15	2·79 m.mol.	1·50 m.mol.	Reaction incomplete.
4·92	5·02	0·05	Almost complete.
4·04	3·99	0·01	Complete.

Discussion.

When carbon tetrachloride hydrolyses, two reactions are possible:

$$2H_2O + CCl_4 = CO + 4HCl \quad \ldots \quad \ldots \quad (i)$$
$$H_2O + CCl_4 = COCl_2 + 2HCl \quad \ldots \quad \ldots \quad (ii)$$

In the first reaction, the production of each mole of carbon dioxide consumes two moles of water, while only half this quantity is required for the second reaction. In the experiment described the carbon dioxide evolved, corresponds to the reaction and so it may be concluded that carbonyl chloride and hydrochloric acid gas are the products of hydrolysis.

Experiments on the adsorptive power of the gel containing residual hydrogen chloride are described in Part II. For comparative studies, instead of silica gel, glass beads were employed in the tube B and nitrogen, saturated with water and carbon tetrachloride vapours were passed over the beads for 3 hours at 100°, 200°, 400° and 500°. Only at 500° a slow production of carbon dioxide was noticed.

The results show that the residual water in the activated gel has remarkable chemical activity in as much as, it can bring about at 110°, the hydrolysis of a comparatively inert substance such as carbon tetrachloride, hydrolysis of which normally begins at 500°. It is possible that the molecules of the residual water in silica gel are so oriented that the hydrolysis of the chloride is favoured. Reference to Table II (column 2) shows that it is possible to remove all the water in activated silica gel, by a prolonged passage of carbon tetrachloride vapour at a suitable temperature.

Summary.

1. Carbon tetrachloride vapour has been found to react with the residual water in activated silica gel. The reaction is perceptible at 110° and takes place at moderate velocity at 300°, forming carbonyl chloride and hydrochloric acid gas.

2. All the water in the activated gel can be removed through this reaction which gives a gel that retains hydrogen chloride very firmly.

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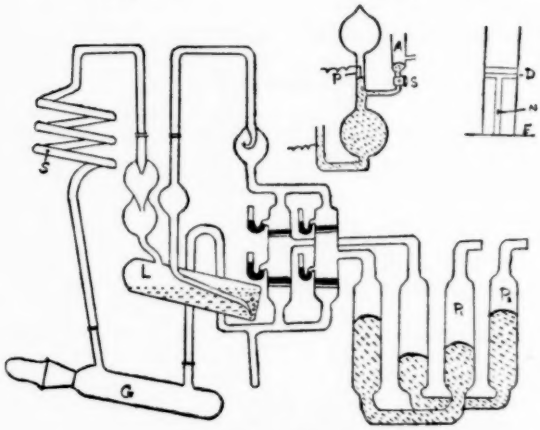
Investigations on the Adsorptive Property of Silica Gel. Part II. Adsorptive Properties of Silica Gel containing Residual Hydrogen Chloride.

By M. R. Aswathanarayana Rao.

Whether residual water is essential for the adsorptive properties exhibited by silica gel is a question that has been investigated by several workers. Patrick and others found that the gel deprived of its water by intense heating suffered considerable loss in its adsorptive properties (*J. Phys. Chem.*, 1927, **31**, 1511 ; 1932, **36**, 475). Rao and Doss (*ibid.*, 1931, **35**, 3487) attempted to prepare gel in which water had been replaced by alcohol but found that such displacement was not complete. In the course of an investigation (Part I, p. 322) on the hydrolysis of carbon tetrachloride by activated silica gel, it was noticed that at the end of the reaction the gel was free from water but held with great firmness about 10% of hydrogen chloride by weight. A study of the properties of this gel was undertaken as being of some importance. The adsorptive capacity of the gel for carbon tetrachloride and its selective adsorption from a mixture of alcohol and benzene were measured.

Experimental.

Fig. 1. Fig. 1*b*. Fig. 1*a*.



All glass circulation pump.

Silica gel in which water had been replaced by HCl, was prepared by the hydrolysis of carbon tetrachloride as described in the previous Part (p. 322). The gel had about 10 % residual HCl. The adsorption was carried out in a closed system using a modification of the circulation pump (Fig. 1) described by B. S. Rao. (*J. Phys. Chem.*, 1932, **35**, 615). In the modified pump the pulsation of mercury column was produced by movement of a metallic piston-reservoir. The pulsations were communicated to the reservoirs P_1 and P_2 by attaching them with a rubber tubing to the metallic reservoirs of the pump. This modification led to a greater convenience in working. Another improvement consisted in the use of mercury valves made out of filter tubes of pyrex, specially prepared in this laboratory. The entire circulation pump was made of pyrex glass. Interchangeable ground glass joints, having accurately ground convex and concave surface (listed in Gallenkamp and Co.) were employed for connecting the pump with the bubbler L, and the gel tube, G. The spiral S, served as a spring and enabled safe connection between G and L.

Preparation of pyrex filter tubes.—Bruce and Bent (*J. Amer. Chem. Soc.*, 1931, **53**, 990) suggested the preparation of pyrex filter tubes the method of which was rather laborious. The following modification was found to be very convenient and highly satisfactory. A pyrex glass tube (Fig. 1 *a*) was slipped on to a nickel disc D, which was rivetted to an iron rod, N ; the latter being supported by a nickel plate E. Pyrex glass powder which had been properly sieved, was moistened and placed on the disc D and carefully pressed. The nickel plate with the glass tube was carefully transferred to an electric furnace. The current was then switched on and the furnace heated to bright redness and the tube was allowed to cool in the furnace. When this procedure was employed it was found unnecessary to have any further sealing of the filter disc to the glass tube.

The circulation pump was fitted up in a large air thermostat, constructed on the lines suggested by Vernon (*Trans. Faraday Soc.*, 1931, **27**, 241). A slight modification was effected in the thermo-regulator as shown in the Fig. 1 *b*. The level of mercury in the regulator could be adjusted by opening the stop-cock S and introducing a glass rod into A, so that at the proper temperature, the mercury in the capillary, just made contact with the electrode P. The stop-cock was then closed. The bulb B was filled with hydrogen so that any sparking at P, caused net fouling of mercury. The following samples of the gel were used for the adsorption of carbon tetrachloride.

TABLE I.

Gel No.	Method of activation.	H_2. (by wt.)	HCl (by wt.)	Adsorption of CCl_4. (by wt.)
1.	Dry air passed over the gel at 300° for 5 hr.	2·73%	...	49·63%
2.	Dry nitrogen passed over the gel for 30 hr. at 300°.	2·45	...	49·27
3.	Dry nitrogen passed over the gel for 30 hours at 400°.	1·70	...	43·51
4.	Dry nitrogen saturated with CCl_4 passed for 30 hrs. at 300°.	9·05	11·08%	43·73
5.	Do. for 30 hrs. at 400°	0·03	8·76	43·2

The carbon tetrachloride vapour was circulated over the gel for one hour, although 80 minutes were usually sufficient for saturating the gel. It was noticed that the hydrogen chloride content of the gel suffered a slight reduction (about 1·5% of gel by weight) when the gel was saturated with carbon tetrachloride with the aid of the circulation pump.

Selective adsorption studies on hydrogen chloride gel.—Methods of measuring selective adsorption (apparent adsorption) have been described by Jones and Outridge (*J. Chem. Soc.*, 1930, 1574), B. S. Rao (*J. Phys. Chem.*, 1932, **36**, 618) and various other workers in the field. The formula used by B. S. Rao is

$$S = m\ (C_1 - C_2) - 100 \log g.$$

where S denotes selectivity ; m, the wt. of the liquid mixture used with the gel ; g, wt. of the gel used; C_1, the initial concentration of the selectively adsorbed liquid and C_2, the equilibrium concentration of the same liquid. The concentrations are expressed in percentages by weight.

During the removal of water from the gel by the hydrolysis of carbon tetrachloride, samples of the gel had to be heated for 30 hours at 300° and 400°. In order to determine the effect of prolonged heating on selective adsorption, samples of the gel were subjected to the same heat treatment as the hydrogen chloride gel, but without contact with carbon tetrachloride vapour. The selective adsorption of the different samples was measured in the following manner.

The benzene used was the C. P. variety which was dried over phosphorous pentoxide and distilled. The absolute alcohol prepared in the usual manner was finally dried over aluminium amalgam and redistilled. Ten mixtures of varying concentrations were prepared and the refractive indices of these mixtures (found by the Pulfrich

refractometer) were plotted against the concentration of alcohol in the mixture. With the help of this curve the unknown concentration C_2 was determined.

Procedure.—The activated silica gel was introduced into a weighed bottle and was weighed again. The bottle was cooled in ice and the binary mixture added. The bottle was reweighed at the laboratory temperature and kept in a thermostat at 30° for 24 hours. The composition of the equilibrium mixture was determined by refractive index measurement as described above. It was found that the presence of hydrogen chloride does not appreciably affect the refractive index measurements. Alcohol was selectively adsorbed at all concentrations. Tables II and III represent the results.

TABLE II.

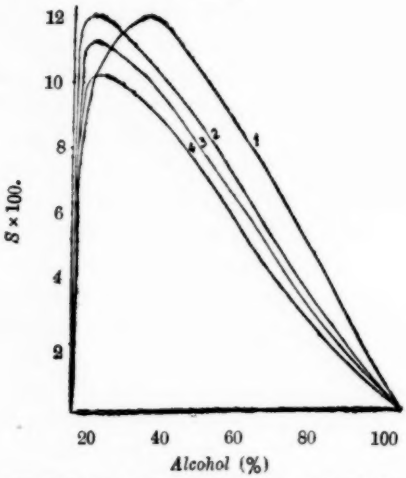
Gel 1.		Gel 2.		Gel 3.	
$C_2 \times 100$.	$S \times 100$.	$C_2 \times 100$.	$S \times 100$.	$C_2 \times 100$.	$S \times 100$.
0·2	0·90	0·2	0·73	0·3	0·29
0·3	5·70	0·4	6·35	0·6	7·10
1·3	10·53	2·0	9·72	2·5	9·17
10·1	11·91	12·8	10·95	12·5	10·36
21·3	10·89	23·2	9·98	23·4	9·17
33·5	9·48	34·5	8·55	35·0	7·79
43·8	7·68	45·2	7·04	45·8	6·14
55·3	5·92	57·0	5·20	57·2	4·40
77·3	2·63	78·5	2·41	78·3	1·06
		87·7	1·11	88·2	1·06
		Gel 1.	Gel 2.	Gel 3.	
H_2O(%) ...		2·73	2·43	1·70	
CCl_4 adsorbed ...		49·63	49·30	47·90	

TABLE III.

Gel 4.		Gel 5.	
$C_2 \times 100$.	$S \times 100$.	$C_2 \times 100$.	$S \times 100$.
0·3	1·05	0·2	0·84
0·6	6·90	0·5	5·58
3·5	7·63	12·0	10·35
12·4	10·90	31·0	12·80
21·7	12·60	41·2	12·40
31·3	12·20	The quantity of the gel was insufficient for more measurements.	
53·5	7·85		
77·0	4·31		
86·0	2·42		
HCl content. ...		11·68	8·5%
CCl_4 adsorption ...		42·73	43·20%

The selectivity-concentration curves given in Fig. 2, indicate change in selectivity caused by prolonged activation and by replacement of water by hydrogen chloride.

FIG. 2.



Curves 1–4 represent $S-C_2$ curve for gel no. 4, 1, 2 and 3 respectively.

DISCUSSION.

From Fig. 2, it is clear that when the gel is heated for 30 hours at 300° and 400°, the selectivity decreases. Hence prolonged heating seems to have a deleterious effect on the surface of the gel causing a diminution in the selective adsorption, though the internal volume of the capillaries in the gel is not appreciably affected. If the gel is ignited in a platinum dish for one hour, the total adsorption of carbon tetrachloride is reduced to 6·5 % while the selective adsorption at its maximum is hardly 0·005. Hydrogen chloride gel takes up less liquid (indicating reduction in capillary space) but the selectivity of the gel is appreciably enhanced.

SUMMARY.

1. Adsorptive properties of silica gel in which residual water has been replaced by hydrogen chloride have been compared with those of ordinary gel.

2. The effect on selective adsorption caused by the prolonged heating of silica gel during activation has been studied.

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Investigations on the Adsorptive Property of Silica Gel. Part III. Volume Changes produced on Displacement of Adsorbed Liquids in Silica Gel by Water.

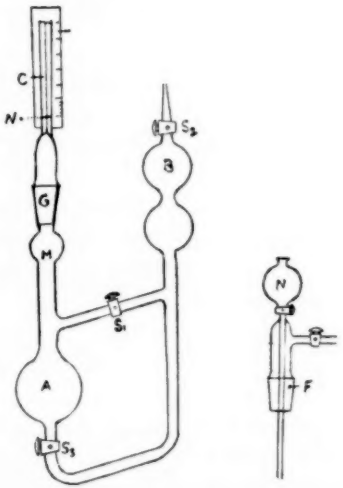
By M. R. Aswathanarayana Rao.

It has been generally assumed that silica gel presents the same volume of capillary space for adsorption of various liquids, though in existing literature on the subject appreciable variations have been noticed by some workers (Holme, "Laboratory Manual of Colloid Chemistry," 1928, p. 195). The exact measurement of adsorption by the usual dynamic method is rather difficult owing to the condensation of the liquid outside the gel capillaries when air saturated with the vapour of the liquid is passed over the gel. The present paper describes the determination of volume changes produced on the displacement of adsorbed liquids in silica gel by water. The volume changes enable us to calculate the volumes of different liquids adsorbed per g. of the gel.

Experimental.

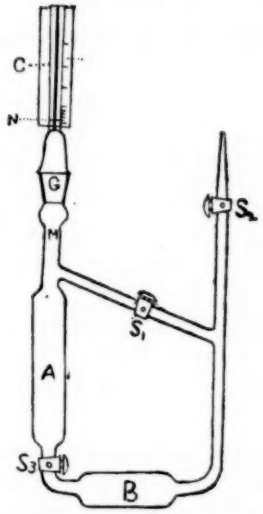
The silica gel used was a commercial product supplied by the Silica Gel Corporation. Its water content was 3·35%. The organic

Fig. 1.



For liquids lighter than H_2O.

Fig. 2.



For liquids heavier than H_2O.

liquids employed were purified and dried by the standard methods in organic chemistry. The volume changes were measured in the apparatus shown in Figs. 1 and 2.

For liquids lighter than water, the apparatus shown in Fig. 1, was employed. The bulb A had a capacity of 120 c.c. The calibrated capillary C, could be attached at G, by an interchangeable ground glass joint. The entire apparatus was first filled with air-free water. Stop-cocks S_1 and S_3 were closed while S_2 remained open. Water in A was then poured out and was dried well by prolonged evacuation using connection F. A weighed amount of the silica gel was introduced into A, through G, which was again fitted with the tube F, and evacuated for an hour. It was then filled with the air-free organic liquid (introduced through the funnel N) to the mark M. F was then replaced by the cappiliary C. The apparatus was immersed in a thermostat at $30° \pm 0·005$ until the stop-cock S_2 was under water and the bulb A was completely filled with organic liquid to the mark N, on the capillary. After allowing the apparatus to attain the temperature of the thermostat, stop-cock S_2 was closed, S_1 opened and the reading taken. When the reading was constant, S_3 was opened to allow the water to wet the gel and the level in C was read. It was noticed that there was a large decrease at first followed by a slight rise as shown in Table I for a typical experiment. When the volume remained contsant for 4 hours, the fiinal reading was taken. The results are shown in Table II.

TABLE I.

Time (min.) ...	15	30	45	60	75	120	600
Decrease in vol. (c.c.) ...	0·582	0·569	0·566	0·560	0·538	0·529	0·518

TABLE II.

Liquid.	Decrease in volume of the gel.	Average.	Correction for volume change on mixing the liquid with water in absence of the gel.
Benzene	0·00850 c.c./g.		
	0·00863	0·00807	Nil
Xylene	0·0109		
	0·0108	0·0109	Nil
Carbon tetra-	0·0200		
chloride	0·0198	0·0199	Nil
Nitro-	0·017		
benzene	0·0198	0·0198	0·007 c.c. per 20·5 g.
Aniline	0·00694		0·038 c.c. per 20·2 g.

The results obtained show clearly that silica gel takes up a larger volume of water than the liquids mentioned above. If in silica gel the capillary space available for occupation of liquids is to be considered constant, we have to assume that water is under great compression and further more that different liquids held in the gel capillaries are subjected to different pressures. It is more probable, however, that in silica gel there are certain fine capillaries which can be penetrated only by water but not by organic liquids and that different organic liquids have different organic penetrating powers, carbon tetrachloride being least active. Certain observations of Cude and Hullet (*J. Amer. Chem. Soc.*, 1924, **46**, 833) are of interest in this connection. They found that active charcoal had maximum density in water. The following results were obtained by them.

TABLE III

Density of charcoal.

Water	Benzene	Carbon tetrachloride
1·629 after 15 min.	1·734 after 15 min.	1·586 after 15 min.
1·654 ,, 119 hrs.	1·797 ,, 286 hrs.	1·647 ,, 386 hrs.

The differences in density are probably due to different penetrating powers.

The volumes of carbon tetrachloride and benzene absorbed per g. of the gel were determined by the dynamic method and found to be 0·3288 c.c. for benzene, and 0·3126 c.c. for carbon tetrachloride. The difference in volumes absorbed is 0·0092 c.c. per g. of the gel. This value compares favourably with the difference in volume decrease noticed in the displacement experiment (*vide*, Table III, 0·0199 − 0·00857 = 0·0113 c.c. per g.).

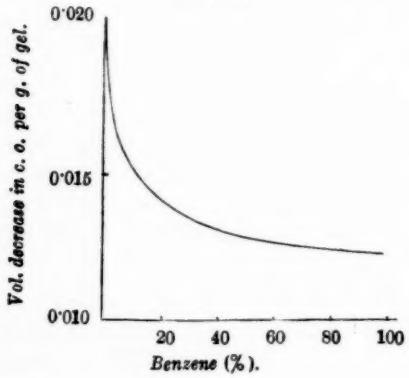
Volume decrease caused when water displaces a mixture on silica gel.—For this investigation, a mixture of benzene and carbon tetrachloride was employed since it was not soluble in water. The experimental procedure was the same as in the previous case; instead of organic liquid, binary mixture was used. The results are tabulated below. The sample of the gel used was different from that employed in the previous experiment and gave a volume decrease of 0·0198 c.c. per. g. of the gel when benzene was displaced by water.

TABLE IV.

Benzene in the mixture.	Vol. decrease.	Benzene in the mixture.	Vol. decrease.
100·0 %	0·0123 c.c./g.	34·6 %	0·0132 c.c./g.
92·4	0·0123	22·4	0·0139
77·5	0·0125	15·9	0·0146
60·0	0·0126	8·2	0·0160
51·3	0·0128	0·0	0·0200

The results are represented in Fig. 3. It is to be noticed that the slope of the curve is greatest at low concentrations of benzene.

FIG. 3.



DISCUSSION.

The defect in the dynamic method of measuring adsorption has already been pointed out. Using the displacement method, described in this paper we can calculate more accurately the volumes of different liquids adsorbed by silica gel, water being employed as the standard liquid. This method would be of particular value when dealing with liquids of low vapour pressure, for which the dynamic method is inapplicable (because the attainment of equilibrium is very slow).

Measurements by the displacement method are not practicable when the liquid dissolves in water producing large changes in volume. The volume decrease in the case of mixtures is of particular interest. If there had been no selective adsorption of benzene from its binary mixture with carbon tetrachloride, the volume decrease for 8% benzene mixture should have been 0·0193 c.c. while it is actually 0·0160 c.c. This shows considerable selective absorption of benzene at low concentrations (*cf.* B. S. Rao, *J. Phys. Chem.*, 1932, **36**, 616). Silica gel is to be considered to have a certain adsorption surface which can be occupied by benzene, but not by carbon tetrachloride. When benzene in 8% concentration is employed, nearly half of this reserved space gets occupied by benzene. At 22 %, nearly 80 % is similarly occupied. This accounts for the slope of the curve in Fig. 3.

Summary.

1. The volume changes produced on displacement by water, of adsorbed liquids in silica gel has been measured using an apparatus specially devised for the purpose.

2. The displacement method described, enables one to calculate the volume of liquids adsorbed per g. of the gel.

3. Unlike the dynamic method, the new technique is applicable to non-volatile liquids.

4. The method has also been used to measure the decrease in volume on the displacememt by water, of binary mixtures adsorbed by the gel and the significance of the results obtained has been discussed.

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Investigation on the Adsorptive Property of Silica Gel. Part IV. Liberation of Air from Silica Gel Capillaries during Adsorption of Liquid.

By M. R. Aswathanarayana Rao.

When activated silica gel adsorbs liquids, the air present in the gel capillaries is liberated. The volume relations between air displaced and the liquid adsorbed are of interest, and have been measured using a slight modification of the apparatus employed in the displacement experiment described in a previous part (p. 331).

Experimental.

In the apparatus shown in Fig. 1 the volume enclosed by the stop-cocks S_1, S_2 and S_3 was carefully filled with water so that no air-bubbles were present (S_2 was kept open). The bulb A, was freed from moisture by evacuation. Activated silica gel (about 4·5 g.) was weighed and introduced into the bulb. The capillary tube C, with the mercury manometer was attached at G, and the apparatus placed in a thermostat at 30° ± 0·01. After the attainment of the temperature of the thermostat, the manometer was read by a travelling microscope. When the pressure in the system was noticed to be constant, stop-cock S_2 was closed and S_3 and S_1 opened. The manometer was read again when the pressure was constant. The results are given in Table I.

Fig. 1.

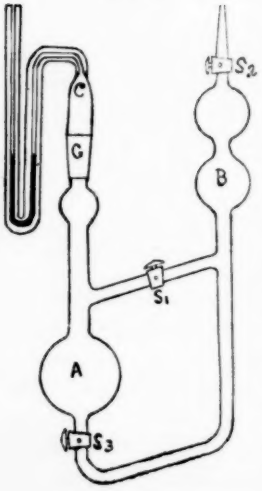


TABLE I.

Time.	Barometric pressure.	Manometer reading.	Pressure in A.
0 min.	68·205 cm.	0·668 cm.	68·873 cm.
5	68·205	5·780	73 985
20	68·205	5·821	74·026
1 hr.	68·285	6·312	74·597
6	68·365	6·257	74·622
10	68·200	6·422	74·622

Calculation of the result.—Pressure change due to the liberation of air = (74·622 − 68·873) = 5·749 cm.

Aqueous tension at 30° = 3·130

Excess pressure due to displaced air = 2·619

Volume of the bulb A, up to the capillary = 99·8 c.c.

Weight of the gel taken = 4·443 g.

Hence, the vol. of air (at 30° and 76 cm. pressure) per g. of the gel

$$= \frac{99{\cdot}8 \times 2{\cdot}69}{4{\cdot}443 \times 76}$$

$$= 0{\cdot}474 \text{ c.c.}$$

A duplicate experiment gave a value = 0·768 c.c. per g.

The average value = 0·771 c.c./g.

The volume of water adsorbed by 1 g. of the gel at saturated vapour pressure = 0·337 ,,

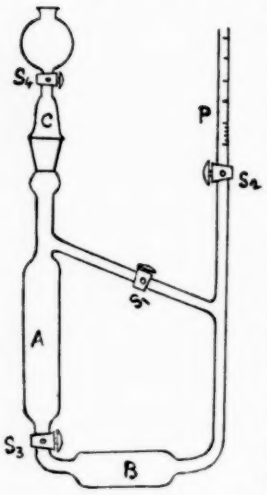
If this volume is taken as the total internal gel volume, the average pressure of the air inside the gel capillaries

$$= \frac{0{\cdot}771}{0{\cdot}337} = 2{\cdot}289 \text{ atmos.}$$

Air liberated when water wets silica gel which is immersed under an organic liquid.—During the displacement of an adsorbed organic liquid by water a certain volume of air is liberated. The volume of

air thus set free was measured using the apparatus shown in Fig. 2.

FIG. 2.



The bulb A, was completely filled with the organic liquid up to the stop-cock S_4. Immersed in this was a weighed quantity of the gel. The space enclosed by the stop-cocks S_1, S_2 and S_3 was filled with water through S_2. As in the previous experiment the apparatus was immersed in a water thermostat till the level of the liquid in the graduated tube P was constant for 30 minutes. On opening S_1 and S_3, water gradually wetted the gel. After about two minutes bubbles of gas appeared round the gel particles and gradually collected at C, causing a corresponding rise in the tube P. The final reading was taken after 15 hours there being no appreciable rise after 10 hours. The results are given in Table II. The air liberated was analysed by standard methods of gas analysis using Ambler's apparatus (*Analyst*, 1929, **54**, 517) and found to contain 16·2% oxygen and 83·8% of nitrogen.

TABLE II.

Liquid displaced by water.	Vol. change during displacement.	Air liberated of gel.	Average pressure of air in corresponding capillary space.
1	2	3	4
Benzene	0·0085 c.c./g.	0·0937 c.c./g.	11·0 atmos.
Nitrobenzene	0·0107	0·1184	11·0
Carbon tetrachloride	0·0200	0·1677	8·5

In this table, column 1 gives the particular organic liquid in which the gel was immersed before wetting with water. In column 2 the volume decreases on displacement of the organic liquid by water (as described in Part III, p. 332) is given. Column 3 represents the volume of air liberated during the displacement of the liquid (in which the gel

was merely immersed without previous evacuation) by water. The result of column 4 is obtained by dividing the volume of air liberated by the volume change.

Discussion.

In the calculation of the results in column 4, Table II, it has been assumed that when the gel is immersed in a liquid like benzene, the space which is not accessible to it (but accessible to water) in the gel is filled up with air under pressure. Another assumption made is that the liquid occupies all the space available for it in the gel, whether the gel is evacuated or not before the introduction of the liquid. Similar results were obtained by Patrick and Opdycke (*J. Phys. Chem.*, 1925, **29**, 601), who state that the amount of sulphur dioxide taken up by silica gel is the same, whether the experiment is done by the static or the dynamic method. On these assumptions it has been shown that when the gel is immersed in a liquid, the air which is present in the gel space (not accessible to liquid) will be at a high pressure, the pressure depending upon the particular liquid used. Thus in the case of benzene the pressure is 11 atmos. while it is 8 atmos. in the case of carbon tetrachloride.

Summary.

1. The volume of air liberated from silica gel (when water wets it) has been measured and it has been shown that the air has an average pressure of two atmos. in the gel space.

2. It has been shown that the average pressure of air inside the gel space when it adsorbs a liquid will be about 10 atmos depending upon the particular liquid.

3. It is suggested that the air in the finest capillaries is held with great tenacity and can only be displaced by water.

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Investigations on the Adsorptive Property of Silica Gel. Part V. The Specific Gravity of Silica Gel under Various Liquids.

By M. R. Aswathnarayana Rao.

Measurements of the apparent density of activated charcoal under various liquids have been carried out by Cude and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 391) and by Harkins and Erving, (*ibid.*, 1921, **43**, 1787). The apparent density of silica gel under water has been measured by Mc Gavack and Patrick (*ibid.*, 1920, **42**, 952). But Duright and co-workers (*ibid.*, 1930, **52**, 4635) have found the true density by making use of helium as the pore-filling substance. The term apparent density usually means the density determined by the displacement of mercury which cannot enter the microscopic and ultra-microscopic pores (*cf.* McBain, "Sorption of Gases and Vapours by Solids," 1932, p. 79), hence the term specific gravity has been used in this paper.

Experimental.

A specific gravity bottle was fitted with accurately ground cap that prevented the loss of liquid by evaporation. The measurements were carried out in a thermstat at 30±° 0·01. A weighed amount of the gel was placed in the specific gravity bottle (the weight of the bottle having been previously determined) and was evacuated by means of the device shown in Fig. 1. The desiccator D, had a funnel F, and a side-tube S, which were connected by means of a ground glass joint at G. The bottom of the funnel passed through the neck of the specific gravity bottle as in the figure. After evacuating the desiccator for an hour (with the gel in the bottle kept in position as in the figure) the liquid was introduced through F, and the gel was allowed to remain with the liquid for 12 hours to attain equilibrium. The bottle was weighed again and the specific gravity was calculated in the usual manner. The following results were obtained.

Fig. 1.

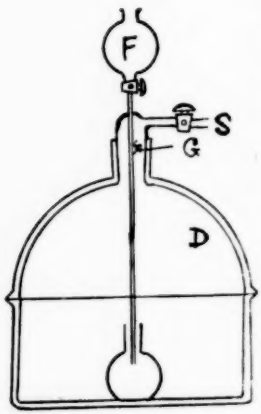

TABLE I

Liquid.	Sp. gr.	Liquid.	Sp. gr.
Water	2·241	Nitrobenzene	2·189
Benzene	2·201	CCl_4	2·127
Xylene	2·189	Aniline	2·195

Duplicate experiments agreed within 0·1 to 0·2%.

DISCUSSION.

That the specific gravity should be greatest in water and least in carbon tetrachloride is to be expected from the fact that in silica gel, water has the greatest penetrating power and carbon tetrachloride the least. This may be gathered from the earlier experiments considered in Part III (p. 332). The question whether the difference in compressibility is responsible for the variation in specific gravity, has been considered by McBain with reference to charcoal in his book (*loc. cit.*, p. 87, 459). There has been a considerable difference of opinion about this subject. If the theory of compressibility is accepted, it will be difficult to explain the liberation of air, when water wets the silica gel immersed in other liquids. The following calculation shows the relationship between the specific gravity and the volume decreases described in part III.

Reference to column 2 of Table II of Part IV (p. 338) gives the displacement effect per g. of the gel. In the case of benzene this is 0·0085 c.c. of the gel space more than the space occupied by benzene. That is 2·24 g. of the gel would appear in water to have a volume of 1 c.c. and in benzene a volume of $1{\cdot}0015 \times 2{\cdot}241 = 1{\cdot}019$ c.c. Hence the specific gravity of the gel in benzene would be $2{\cdot}241/1{\cdot}019 = 2{\cdot}200$. That is, the calculated value for the specific gravity of the gel in benzene is 2·200 where as the observed value is 2·202 as shown in Table I. The agreement between the calculated and the observed values can be gathered from the following table.

TABLE II.

Liquid.	Specific gravity.	
	Calc.	Obs.
Benzene	2·200	2·202
Xylene	2·190	2·189
Nitrobenzene	2·189	2·189
CCl_4	2·140	2·127
Aniline	2·197	2·195

The agreement between the theoretical and the observed values is quite satisfactory except in the case of carbon tetrachloride, where the experimental errors were appreciable owing to the high volatality of the heavy liquid. It is interesting to note that in spite of the fact that the correction for volume change on mixing aniline (Table II, Part III, p. 332) is quite appreciable in the displacement experiment, yet the valve for aniline agrees well with the calculated one. It is worthy of notice that the specific surface of silica gel is $5{\cdot}0 \times 10^6$ for water adsorption and $4{\cdot}3 \times 10^6$ per sq. cm. for organic liquids as calculated by Bartell and Fu ("Colloid Syposium Annual," Vol. VII, p. 144). This means that silica gel offers a larger area to water than to organic liquids. This is in agreement with the observation that silica gel has the greatest specific gravity in water.

SUMMARY.

All the experimental observations noted, the volume changes on displacement of adsorbed liquids by water, the values for the volume of air liberated and those for the specific gravity of silica gel in different liquids can be satisfactorily explained on the basis of the assumption that liquids vary in their power of penetrating into the capillaries present in silica gel, water having the greatest penetration and carbon tetrachloride the least.

The author wishes to thank Mr. K. Subbaramiah for experimentally checking the accuracy of some of the work described in parts IV and V and to Professor B. Sanjiva Rao for kind criticism during the course of the investigation and for the valuable help in preparing the papers for publication.

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Halogenation. Part X. Iodination of Xylenes and Mono-iodoxylenes.

By Phuldeo Sahay Varma and K. S. Venkat Raman.

In the present communication we have described the iodination of the three xylenes and their mono-iodo derivatives (*cf.* Varma and others, *J. Indian Chem. Soc.*, 1926, **3**, 291, 342). The mono-iodo-xylenes can be prepared in better yields in presence of nitro-sulphonic acid mixture containing about 50% fuming nitric acid. The di-iodo derivative can be obtained both by the iodination of the respective xylenes themselves and the mono-iodo-xylenes. The di-iodo-derivatives of *o*- and *p*- xylenes have been prepared for the first time and their constitution has been suggested only from analogy with the corresponding chloro and bromo compounds as 4:5-di-iodo-*o*-xylene and 2:5-di-iodo-*p*-xylene.

Experimental.

4-Iodo-o-xylene.—A mixture of *o*-xylene (15 c.c.), powdered iodine (15 g.) and acetic acid (10 c.c.) was heated on a sand bath in a flask with a reflux condenser and a mixture of fuming nitric and nitro-sulphonic acids (7 c.c.) was added to it drop by drop in about 10 minutes and the heating continued for about 20 minutes more. The product was washed free of iodine by 5% sodium hydroxide solution and steam distilled. The pinkish oil was separated, dried over fused calcium chloride and distilled. The fraction distilling between 228-35° was found to be almost pure 4-iodo-*o*-xylene (21 g.) and the residue in the flask contained traces of nitro-*o*-xylene.

m-Xylene and *p*-xylene under foregoing treatment yielded 4-iodo-*m*-xylene (74%) and 2-iodo-*p*-xylene (65%) respectively. In both cases nitroxylene was also obtained in very small quantity.

4:5-Di-iodo-o-xylene—(*i*) From *o-xylene*—To a mixture of *o*-xylene (10 c.c.), iodine (18 g.) and acetic acid (20 c.c.) in a flask heated on a sand bath, nitro-sulphonic acid mixture (10 c.c.) was added drop by drop in about half an hour and the reaction mixture heated further for about 5·5 hours. The flask was then cooled, the product washed with a dilute solution of sodium hydroxide till free from iodine, dried over fused calcium chloride

and then cooled in a freezing mixture of ice and salt at about −20° when plate like crystals separated out. It was filtered in the cold and was recrystallised first from carbon tetrachloride and then from ether, m.p. 73°. (Found: I, 68·89 $C_8H_8I_2$ requires I, 70·93 per cent). It is easily soluble in carbon tetrachloride, chloroform, carbon disulphide, benzene and ether ; very sparingly soluble in cold absolute alcohol ; slightly soluble in glacial acetic acid in the cold but more on warming.

(*ii*) From 4-*iodo*-o-*xylene*.—To a mixture of 4-iodo-*o*-xylene (6 c.c.), iodine (7 g.), acetic acid (5 c.c.) and carbon tetrachloride (5 c.c.) heated on a sand bath to about 170°, nitro-sulphonic acid mixture (5·5 c.c.) was added in about 15 minutes and the heating continued for about 1 5 hours more, the temperature of the bath being maintained at about 235°. The reaction product was then subjected to the same treatment as in the preceding experiment, yield 6·2 g.

4 : 6-di-iodo-*m*-xylene (m.p. 72°) can be obtained from *m*-xylene or from 4-iodo-*m*-xylene in a similar manner. This compound is identical with the 4 : 6-di-iodo-*m*-xylene prepared by Hammerich (*Ber.*, 1890, **23**, 1635) and Tohl (*Ber.*, 1893, **26**, 1105).

2 : 5-*Di-iodo*-p-*xylene* (*i*) From p-*xylene*.—To *p*-xylene (10 c.c.), iodine (20 g.), and acetic acid (15 c.c.) heated on a sand bath, nitrosulphonic acid mixture (12 c.c.) was added in proportions of 2 c.c. at a time in about an hour. The flask with its contents was further heated to about 220° for about 5 hours. The solid product was separated as described before, m.p. 104°. (Found: I, 69·74. $C_8H_8I_2$ requires I, 70·93 per cent). The solubility is the same as in the case of 4 : 5-di-iodo-*o*-xylene.

(*ii*) From 2-*iodo*-p-*xylene*.—To 2-iodo-*p*-xylene (10 c.c.), powdered iodine (12 g.) and acetic acid (10 c.c.) in a flask heated on a sand bath, nitrosulphonic acid mixture (6 c.c.) was added drop by drop in about half an hour and the heating continued for about 2·5 hours. The product was worked up as described in the previous experiments, yield 12·3 g.

This compound has further been obtained by putting together 2-iodo-*p*-xylene (5 c.c.) and concentrated sulphuric acid (14 c.c.) in a test tube and allowing them to stand for 9 weeks. Crystals of the di-iodo derivative (1·8 g.) separated out.

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Selective Adsorption and its Significance. Part I. Nature of Selective Adsorption.

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A number of workers have determined selective adsorption on porous substances from binary mixtures (Williams, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, 2, No. 23; Ostwald and Izaguirre, *Kolloid Z.*, 1922, **30**, 279; Patrick and Jones, *J. Phys. Chem.*, 1925, **29**, 1; Bartell and Scheffler, *J. Amer. Chem. Soc.*, 1931, **53**, 2507; Jones and Outridge, *J. Chem. Soc.*, 1930, 1574; B. S. Rao, *J. Phys. Chem.*, 1932, **36**, 615). The selective adsorption may be expressed as

$$S = \frac{m}{g} (C_1 - C_2) \quad \ldots \qquad (i)$$

where S denotes selectivity; m, wt. of the liquid mixture used; g, wt. of the silica gel in equilibrium with the liquid mixture; C_1, the initial conc. of the selectively adsorbed component expressed in wt. fraction; and C_2, the equilibrium conc. of the selectively adsorbed component expressed in wt. fraction.

Williams (*loc. cit.*) uses a similar formula but calls S, the "Apparent adsorption". Bartell and Scheffler (*loc. cit.*) employ a similar formula but express C_1 and C_2 in mole fractions. S is then termed "Molar selectivity". All these equations give the same type of curve when S is plotted against the equilibrium concentration, C_2. In this paper an attempt is made to explain the values of selectivity obtained with two samples of silica gel.

Experimental.

Gels used.—Two types of silica gel A, and B were prepared. Gel A was prepared by Patrick's method (*J. Amer. Chem. Soc.*, 1920, **42**, 951). In the case of the gel B, the precipitate of silicic acid, which appeared during the addition of the sodium silicate solution to hydrochloric acid did not disappear completely. The jellies that were so obtained were washed with distilled water, till the washed liquid gave no test for chloride. The washed jellies were dried by passing warm air and finally activated in a current of dry air at 360° for 5 hours. Gel A had the usual *glassy* appearance while gel B was *opaque*. The water

content of the gels was determined by igniting the samples in a platinum crucible at blast lamp temperature; the gel A yielded 3·35% of water while B gave 3·64%.

Benzene, carbon tetrachloride and heptane :—The C. P. liquids were dried over phosphorus pentoxide and distilled.

Absolute alcohol was dried over aluminium amalgam and distilled. Pyridine was dried over caustic potash and distilled. All these liquids showed no change of refractive index when treated with the activated gel.

Selective adsorption at 30° was determined by the method described by B. S. Rao. (*loc. cit.*). The following mixtures were used: (1) Alcohol—benzene, (2) Alcohol—carbon tetrachloride, (3) Benzene—heptane, and (4) Pyridine—heptane. The composition of the equilibrium mixtures was determined by means of a Pulfrich refractometer. The results are given below. In the tables C_2 represents the equilibrium concentration of the selectively adsorbed liquid ; S, the selectivity as calculated from equation (*i*) and $\psi = \frac{S}{1-C_2}$ whose significance is described later.

TABLE I.

Benzene—alcohol.

Alcohol as the selectively adsorbed liquid

Gel A.			Gel B.		
$C_2 \times 100$.	$S \times 100$.	$\psi \times 1000$.	$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.
0·2	6·3	6·3	0·4	10·3	10·3
0·4	12·8	12·8	1·2	15·2	15·3
2·6	19·0	19·5	2·8	18·9	19·4
6·1	20·4	22·2	8·6	20·5	22·4
11·0	20·2	22·7	13·8	19·1	22·2
18·4	18·9	23·1	20·3	17·6	22·2
42·6	12·1	21·9	43·8	11·1	19·6
68·6	5·36	17·1	69·0	5·2	19·2
84·6	2·4	14·7	84·4	2·7	17·0
94·1	0·3	5·5			

TABLE II.

Alcohol—carbon tetrachloride.

Alcohol as the selectively adsorbed liquid.

Gel A.			Gel B.		
$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.	$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.
0·2	18·4	18·5	1·7	20·5	20·9
4·8	22·9	24·0	7·0	21·2	23·8
9·2	22·7	24·3	11·0	20·6	23·2
20·6	18·1	22·8	23·0	16·7	21·7
41·8	12·6	21·6	44·0	11·3	20·1
67·8	5·5	17·2	68·8	4·7	15·1
86·8	1·5	11·4	87·6	1·0	7·7
95·2	0·5	10·0	95·2	0·3	6·3

TABLE III

Benzene—heptane.

Benzene as the selectively adsorbed liquid.

Gel A.			Gel B.		
$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.	$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.
2·0	4·3	4·4	2·2	3·8	3·9
4·8	6·6	6·8	8·2	8·4	9·12
7·0	7·8	8·4	12·0	10·1	11·5
10·6	9·7	10·9	21·0	12·1	15·3
41·8	11·5	19·8	44·0	11·1	19·8
64·4	7·6	21·4	67·0	7·2	21·8
80·4	4·6	22·9	94·6	0·8	14·8
94·3	1·1	18·6			

TABLE IV.

Pyridine-heptane.

Pyridine as the selectively adsorbed liquid.

	Gel A.			Gel B.	
$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.	$C_2 \times 100$.	$S \times 100$.	$\psi \times 100$.
0·1	11·8	11·8	0·2	14·6	14·6
4·3	26·3	27·4	5·9	26·6	28·3
7·0	27·5	37·2	15·1	27·4	32·3
16·7	29·2	35·1	23·2	26·8	34·9
33·6	25·6	38·5	37·1	23·3	37·0
49·0	19·5	38·1	51·2	17·3	35·4
60·0	15·3	38·2	61·0	13·8	35·3
76·5	8·6	36·6	79·7	6·7	32·9
88·0	4·1	34·6	89·1	3·62	33·6

The results otbained have been indicated graphically in Figs. 1-4. It will be noticed that the alcohol is preferentially adsorbed (Figs. 3 and 4) over the entire range from its binary mixtures with benzene and carbon tetrachloride. Pyridine and benzene (Fig.1) are preferentially adsorbed from their binary mixtures with heptane. In general, gel A exhibited higher selectivity than gel B. In benzene—heptane mixtures, however, (Fig. 1) the two selectivity curves were almost identical (this has been explained later). The adsorption of pyridine from the heptane mixtures, however, (Fig. 1) is of particular interest since it displays the highest selectivity of all the mixtures tried hitherto.

DISCUSSION.

The results obtained may be explained on the assumption that the adsorption of the liquids on silica gel is of two kinds, *viz.* (*a*) The adsorption on the surface of the gel, and (*b*) the capillary condensation. Jones and Outridge (*loc. cit.*) have suggested that the liquid held in the capillaries is identical in composition with the bulk liquid. The selectivity phenomenon noticed, seems, therefore, to be entirely due to the adsorption on the surface.

With Langmuir we can assume that the adsorption at the gel surface, is unimolecular; in other words the influence of the surface forces will be confined only to molecules adjacent to the walls of the solid. In the case of selective adsorption with alcohol-benzene mixtures, although both the liquids are adsorbed on the gel surface, the amount of alcohol present at the surface will be greater than the amount of benzene. This may be due to the greater attraction of the silica surface for the more polar liquid.

A relationship can be deduced between selectivity and the amount of alcohol held at the silica surface. Let 1 g. of the gel adsorb m' g. of the liquid mixture at the equilibrium concentration C_2. Suppose a portion m_1 of this mixture is held at the surface while the remainder $(m'-m_1)$ is condensed in the capillaries. Let C_u be the concentration of alcohol in m_1 and C_g in m' the total liquid adsorbed. Then the total alcohol adsorbed per g. of the gel

$$= m' \; C_g = m_1 \; C_u + (m' - m_1) \; C_2$$

Hence $$m' \; (C_g - C_2) = m_1 \; (C_u - C_2)$$

It has been shown (effect of temperature on selective adsorption, Eq. *ii*) that

$$S = m' \; (C_g - C_2) \quad \ldots \quad \ldots \quad \ldots \quad (ii)$$

Therefore, $$S = m' \; (C_g - C_2) = (C_u - C_2) \; m_1 \quad \ldots \quad (iii)$$

Thus selectivity represents the excess of alcohol present at the surface of 1 g. of the gel (owing to the selective nature of adsorption) over what would have been present if the bulk concentration had continued right up to the surface.

Suppose the excess of alcohol ψ is removed from m_1, then the remaining mixture $(m_1 - \psi)$ will have a concentration C_2

i.e., $$m_1 \; C_u = \psi + (m_1 - \psi) \; C_2$$

or $$\psi \; (1 - C_2) = m_1 \; (C_u - C_2) = S \text{ (by Eq. } iii) \quad \ldots \quad (iv)$$

or $$\psi = \frac{S}{1 - C_2} \quad \ldots \quad \ldots \quad \ldots \quad (v)$$

Thus ψ the excess of alcohol at the surface can be calculated from known values of S and C_2. A similar equation has been derived by Williams (*loc. cit.*) for U_0, the " apparent adsorption".

$$U_0 = M\,(C_0 - C)/G(100 - C) \quad \ldots \quad \ldots \quad (vi)$$

where M denotes wt. of the binary mixture; G, wt. of the gel in equilibrium mixture; C_0, the initial conc. of the solute expressed in % by wt; and C, the equilib. conc. of the solute in % by wt.

If the concentration, C is expressed in weight fraction, this equation will be identical with the one that is obtained for ψ. But instead of representing ψ as the excess of alcohol taken by the surface, Williams considers U_0 as the true adsorption of the solute when no solvent is adsorbed but in practice both the liquids of the binary mixture are adsorbed. Hence the interpretation of ψ as the excess of alcohol taken up by the gel gives a better picture of the phenomenon.

The true adsorption (the total weight of alcohol taken up by the gel from the mixture) can be easily calculated by the selectivity data. Williams (*loc. cit.*) has calculated the true adsorption of alcohol on the gel by making use of the two equations

$$U = U_0 + WC/100 - C \quad \ldots \quad \ldots \quad \ldots \quad (vii)$$

and

$$I = W + U \quad \ldots \quad \ldots \quad \ldots \quad (viii)$$

where U = wt. of the solute adsorbed when the equilib. conc. is C; W, wt. of the solvent in the same condition; I, total wt. of the solute and the solvent. I is determined experimentally by finding out the weight of the mixture adsorbed in the vapour phase at the equilibrium concentration. Jones and Outridge (*loc. cit.*) assumed that the internal gel volume is constant and calculated I for *n*-butyl alcohol and benzene mixtures by the equation

$$I = V\,D \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (ix)$$

where V denotes the internal gel volume, and D, the density of the solution within the gel.

Assuming that the density-concentration curve of *n*-butyl alcohol and benzene is almost a straight line, D is calculated by a method of successive approximation. The authors determined V by experiment and noticed a slight variation of V with different liquids. This they attributed to the exprimental error. The validity of this assumption has been more vigorously studied by the present author (compare, p. 331). It is found that in the case of mixtures, only about a

certain concentration, the volume of the liquid taken up by the gel will be that of the preferentially adsorbed liquid.

The true adsorption can be calculated from the selectivity data in a simpler manner. Let Q be the weight of alcohol taken up by the gel when in equilibrium with the saturated vapour of alcohol, then the total internal gel volume for alcohol

$$= \frac{Q}{D_A} \text{ where } D_A \text{ is the density of alcohol.}$$

The volume of the adsorbed liquid having concentration C_2

$$= \frac{Q-\psi}{D_A} = m' - \psi$$

where m' is total amount of the liquid adsorbed (*cf.* Eq. *ii*). The true adsorption of alcohol (*i.e.*, the total amount in m')

$$= C_2(m'-\psi)+\psi = C_2(Q-\psi)\frac{D'}{D_A}+\psi \quad \ldots \quad \ldots \quad (x)$$

where D' is the density of the mixture at a concentration C_2. Similarly " True adsorption " U of benzene

$$= (1-C_2)(Q-\psi)\frac{D'}{D_A} \quad \ldots \quad \ldots \quad \ldots \quad (xi)$$

The above method of calculating the true adsorption is simpler than that employed by Jones and Outridge, (*loc. cit.*) as it does not involve the calculation of D (density of the adsorbed liquid) by the method of successive approximations.

It is of interest to note that in binary mixtures of *n*-butyl alcohol and benzene investigated by Jones and Outridge (*loc. cit.*, p. 1580, Table II) the apparent adsorption x/m is equal in magnitude to the true adsorption U. This follows from the fact that the true adsorption

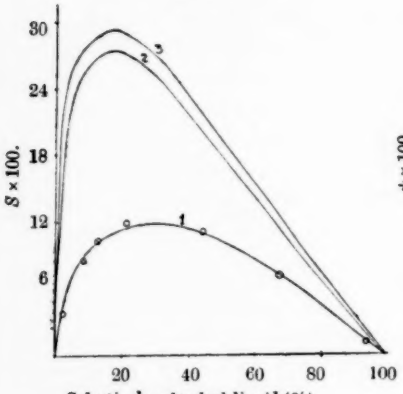
$$= C_2(Q-\psi).\frac{D'}{D_A}+\psi = C_2\psi.\frac{D'}{D_A}+\psi\left(1-C_2\frac{D'}{D_A}\right) \quad \ldots \quad (xii)$$

At low concentrations, C_2 is very small in comparison with ψ so that the factors containing C_2 may be neglected. Hence the true adsorption

$$= \psi = \frac{S}{1-C_2} = S.$$

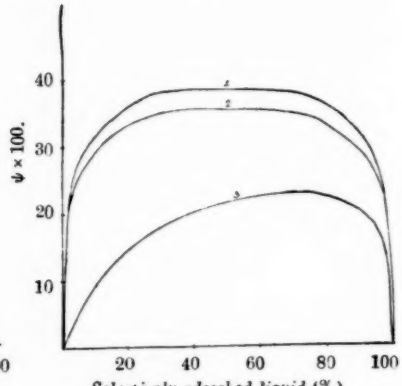
Thus Jones and Outridge get U almost equal to S till C_2 reaches a value of 2%.

FIG. 1.



1 and 2 for benzene-heptane and pyridine-heptane mixtures with gel A ; 3 for that of latter mixture with gel B.

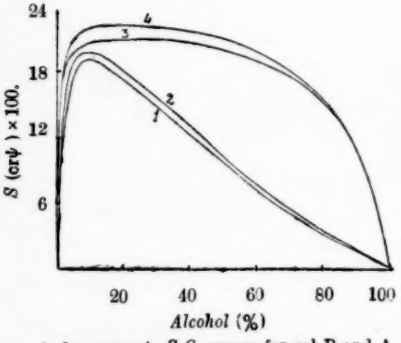
FIG. 2.



1-3 for ψ-C_2 curves for gel A, gel B and gel A + B respectively in pyridine-heptane mixture.

FIG. 3.

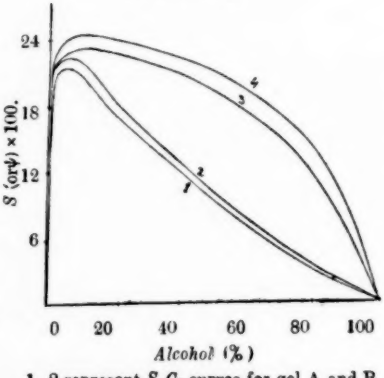
Benzene-alcohol.



1, 2 represent S-C_2 curves for gel B and A respectively.
3, 4 represent ψ-C_2 curves for gel B and A respectively.

FIG. 4.

Alcohol-CCl_4



1, 2 represent S-C_2 curves for gel A and B respectively.
3, 4 represent S-ψ curves for gel B and A respectively.

In Tables I to IV, the values of ψ are given for different mixtures. When these are plotted (Figs. 1-4) it is seen that in the case of pyridine-heptane, the curve is almost horizontal between 30 and 70%

concentration of pyridine. The slope of $\psi - C_2$ curves increases in benzene-alcohol mixtures (Fig. 3) and is greatest in the benzene-heptane mixtures (Fig. 2). The horizontal portion of $\psi - C_2$ curve in the case of pyridine-heptane mixtures is of particular interest. If from the horizontal portion of the curve, ψ values at concentrations C'_2 and C''_2 are taken, we have

$$\psi = \frac{S'}{1-C'_2} = \frac{S''}{1-C''_2}$$

where S' and S'' are the selectivity values at C'_2 and C''_2, respectively. Substituting for S in equation *(iii)* we get

$$\frac{m'_1(C'_u - C'_2)}{1-C'_2} = \frac{m''_1(C''_u - C''_2)}{1-C''_2}$$

where m'_1 and m''_1 are the weights of the mixtures on the gel surface at C'_2 and C''_2; C'_u, C''_u are the concentrations of alcohol at the surface for the equilibrium concentrations C'_2 and C''_2. The difference in the value between m'_1 and m''_1 is negligible.

So $$\frac{C'u - C'_2}{1-C'_2} = \frac{C''u - C''_2}{1-C''_2} \quad \ldots \quad \ldots \quad (xiii)$$

This relationship can only be satisfied if the values of C_u' and C_u'' are very nearly to unity. In other words, the horizontal curve is obtained when the unimolecular layer at the gel surface consists of almost entirely of the selectively adsorbed component. If the value of C_u decreases, the slope of the $\psi - C_2$ curve increases. Thus the slope of the $\psi - C_2$ curves obtained with the two mixtures pyridine-heptane and benzene-heptane gives us an idea of the relative richness of the surface layer in the selectively absorbed component.

The anomalous behaviour of the two gels in the case of benzene-heptane mixtures can be satisfactorily explained. It has been shown by the author that silica gel adsorbs per g. of the gel a larger volume of pyridine (and other liquids like water and alcohol) than of liquids like benzene and heptane. The latter two are adsorbed in equal quantities at the surface of both the gels. Hence there is no appreciable difference in the selectivity values for the two gels with benzene-heptane mixtures. In the case of pyridine-heptane mixtures, different quantities of pyridine are adsorbed at the surfaces

of the two gels. Therefore a difference is noticed in the selectivity values for the two gels. In other words the two gels present the same amount of surface for benzene in the case of benzene-heptane mixtures, but different amounts of surface for pyridine in the case of pyridine-heptane mixtures.

Selectivity measurements can be employed for the comparison of the specific surfaces of different varieties of silica gel. Let S_a and S_b be the selectivity values of two types of silica gel at the same equilibrium concentration C_2 in an alcohol-benzene mixture. It has been shown by the author (Eq. *iii*) that $S = m_1(C_u - C_2)$

$$\text{Therefore} \qquad \frac{S_a}{S_b} = \frac{m_a(C_{ua} - C_2)}{m_b(C_{ub} - C_2)}$$

where m_a and m_b and the wt. of the mixture taken by 1 g. each of gel A and gel B at the surface respectively ; C_{ua} and C_{ub}, the concentrations of alcohol (wt. fraction) at the surface of the gel A and gel B. The difference in adsorptive capacity of the two gels is to be attributed to the difference in silica surface per g. of the gel. The adsorption per sq. cm. of the surface is considered to be the same for both the gels at the same equilibrium concentration C_2.

Therefore, $\qquad C_u$ for A $= C_u$ for B or $C_{ua} = C_{ub}$

Hence $\qquad S_a/S_b = m_a/m_b = A_a/A_b$

where A_a and A_b represent the areas per g. of the two gels. Thus by determining the selectivity of the two gels at the same equilibrium concentration, the ratio of the specific areas can be found out. In the following tables the ratio of selectivity of the gels A and B are given.

TABLE V.

	Pyridine-heptane.			Alcohol-carbon tetrachloride.			Alcohol-benzene.		
C_2.	S for gel A.	S for gel B.	S_a/S_b.	S for gel A.	S for gel B.	S_a/S_b.	S for gel A.	S for gel B.	S_a/S_b.
0·20	0·290	0·264	1·08	0·184	0·176	1·05	0·184	0·176	1·04
0·25	0·281	0·266	1·06	0·168	0·162	1·04	0·170	0·163	1·04
0·30	0·269	0·252	1·07	0·156	0·149	1·04	0·155	0·148	1·03
0·35	0·251	0·237	1·06	0·142	0·135	1·05	0·140	0·135	1·04
0·40	0·230	0·218	1·06	0·129	0·122	1·05	0·127	0·121	1·05

Since the two selectivity curves are almost identical in the case of benzene-heptane mixtures, the ratio of the selectivity is unity at all concentrations.

The ratio S_a/S_b is fairly constant for each binary mixture. It is highest for pyridine-heptane mixtures and is almost identical for the binary mixtures of alcohol with benzene and carbon tetrachloride. It has already been pointed out that the ratio is unity for benzene-heptane mixtures.

Summary.

1. On the basis of the assumption that the liquid held in the capillaries of silica gel, is identical in composition with the bulk liquid, while that adsorbed at the gel surface is responsible for the selectivity noticed, a method of calculating the true adsorption of each constituent has been developed.

2. A method for calculating the excess of the component adsorbed at the surfaces is also presented.

3. Finally the selectivity measurements have been employed in comparing the specific surfaces of two varieties of silica gel.

The author wishes to express his indebtedness to Professor B. Sanjiva Rao for kind and helpful criticism. Grateful thanks are also due to Mr. K. S. Gururaja Doss for his instructive discussions on the subject.

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Oxidation of Sugars by Air in presence of Ceric Hydroxide Sol and Cerous Hydroxide Gels.

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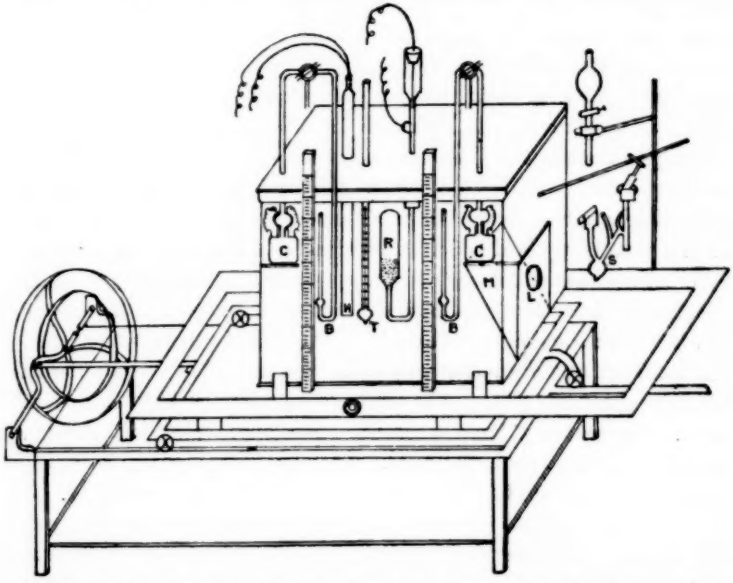
The oxidation of carbohydrates, specially, simple hexoses, by molecular oxygen is a problem of great physiological importance. In strong alkaline medium, sugars are readily oxidised but within the range of p_H found in living organism, hexoses are very resistant to oxidation by air in absence of catalyst. Sphuer (*J. Amer Chem. Soc.*, 1924, **46**, 1494 ; 1926, **48**, 236) has, however, shown that in presence of sodium ferro-pyrophosphate, glucose is slowly attacked by air. The mechanism of oxidation is based on alternate oxidation and reduction of ferrous ion. Dhar and co-workers (*J. Phys. Chem.*, 1925, **29**, 376, 799 ; 1926, **30**, 939 *et seq.*) have studied the problem of oxidation of various carbohydrates and sugars by air. These oxidations were carried out in presence of certain freshly precipitated metallic hydroxides, *e.g* , cerous, ferrous and manganous hydroxides, etc. Two very striking conclusions were arrived at by them from



M—Mirror at 45° ; *B*—Manometer ; *R*—Temp. regulator ; *C*—Cell ; *T*—Thermometer ; *S*—Point-o-lite lamp ; *L*—Lens ; *H*—Heater.

these experiments, namely, (*i*) all sugars are readily oxidised to CO_2 and H_2O by air directly in presence of these hydroxides ; and (*ii*) these hydroxides behave as simple inductors, the reaction between oxygen and glucose coming to an end when these have been completely oxidised.

No attempt has, however, been made to study the kinetics of these oxidations. It was felt that studies on the dynamics of heterogeneous oxidation processes in presence of catalysts might lead to an explanation of the mechanism of the reaction ; and in the present paper, results of such investigations are recorded.

Experimental.

Apparatus.—The apparatus used in the present investigation is a modification of the Barcroft-Warburg apparatus for respiration. The nucleus of the whole apparatus consists of two glass vessels as shown in the diagram in p. 357. These reaction cells are provided with optically plane bases and are connected to simple manometers by a set of stop-cocks for introducing and evacuating gases. The cells are kept completely immersed in water in an electrically regulated thermostat which was shaken by means of wheels over parallel rails. The shaking ensures efficient stirring of the water of the thermostat and also a thorough mixing of air and reactant mixture inside the cells, which admittedly is essential for heterogeneous reactions. To investigate the effect of illumination, a window was cut out in the thermostat and sealed with a lens, at the focus of which remains a point-o-lite quartz mercury lamp. The reaction cell inside the thermostat was tightly held by a circular metal clamp and below it was fixed in the thermostat a glass mirror at an angle of 45° to the path of light. The parallel rays from the lens are reflected by the mirror and fall perpendicularly on the plane bottom of the reaction cell. The infra-red and ultraviolet radiations are cut off by transmission through water and glass. The whole arrangement is kept in a dark room. The mercury lamp is run at a constant current of 2·2 amp. from a storage battery of 30 volts. The absorbed radiation is determined by means of Moll thermopile and a Moll galvanometer. A NaCl solution coloured red with a dyestuff has been used as manometric liquid. The experimental arrangement is given in the diagram.

Oxidations have been carried out with the aid of (*i*) colloidal ceric hydroxide ; and (*ii*) freshly precipitated cerous hydroxide.

Oxidation of Glucose and Laevulose in presence of Ceric Hydroxide Sol.

In each experiment, a 15 c.c. mixture of the composition (5 c.c. of sugar solution, 5 c.c. of sol, 5 c.c. of dilute alkali) is introduced into the cell and the pressure-drop due to absorption of oxygen is noted from time to time in the manometer. A balance cell is also used containing all the solutions except sugar, serving as a thermo-barometer. The colloidal solution is extremely sensitive to any electrolyte and the use of any buffer solution is impossible. Very dilute alkali solutions are used for effecting variation of alkalinity. The p_H value practically remained constant for a period of five hours which was the average duration of the experiment. For p_H up to 9·6, no oxidation is observed during 5 hours in absence of the sol. The ceric hydroxide sol is prepared according to the method of Mata Prasad (*J. Indian Chem. Soc.*, 1932, **9**, 153). The volume of oxygen absorbed at N. T. P. can be easily determined from the simple formula,

$$r = \frac{(V-v).\ x.\ d_1\ 1000 \times 273}{760 \times d_2 \times (273+t)}$$

where, V denotes total capacity of the cell ; v, volume of solution introduced; x, concentration of oxygen in the gas inside the cell; d_1, density of manometer-liquid; d_2, density of mercury; r, total pressure-drop in any given time; and t, temperature at which reaction is carried out.

One set of experimental observation is recorded in Table I to indicate how the velocity constants have been calculated.

TABLE I.

(*In darkness*)

Laevulose=1 %. Conc. of sol=0·016M (*i.e.*, gram mol. of ceric hydroxide per litre in the state of suspension). p_H = 6·6. Temp. = 37·6. Rate of shaking = 45 times a min. Amplitude of oscillation = 9 inches.

Time.	Pressure-drop in Reaction cell.	Balance cell.	Total pressure-drop.	r=c. mm of O_2 ≡ Pr. drop.	$K_c \times 10^3$.
30 min.	0	0	0	—	—
90	9	−1	10	130	—
150	20	4	16	208	0·0022
210	25	4	21	273	0·0019
270	35	8	27	351	0·0020
330	29	−4	33	429	0·0021
390	41	3	38	494	0·020
				Mean	0·0020

TABLE II.

Oxidation of laevulose.

Temp. = 37·6°.

Shaking per min.	O_2 conc.	p_H.	Sol conc.	Conc. of laevulose.	$K_0 \times 10^2$ in Dark.	$K_0 \times 10^2$ in Dark & light.	Quantum yield.
45 times	20%	8·6	0·016 *M*	0·33%	0·0035	0·0040	0·45
,,	,,	,,	,,	1	0·0036	0·0043	0·63
,,	,,	,,	,,	4	0·0036	0·0046	0·90
,,	,,	,,	0·009 *M*	0·28	0·0027	0·0036	0·80
,,	,,	,,	0·016	,,	0·0035	0·0040	0·45
,,	,,	,,	0·025	,,	0·0039	0·0045	0·52
,,	,,	,,	0·016	1	0·0036	0·0043	0·63
,,	,,	6·6	,,	,,	0·0020	0·0032	1·08
,,	4%	8·6	0·016	,,	0·0035	0·0038	0·30
,,	20%	,,	,,	,,	0·0036	0·0043	0·63
,,	100%	,,	,,	,,	0·0036	0·0042	0·54
45	20%	,,	,,	,,	0·0036	0·0043	...
80	,,	,,	,,	,,	0·0047	...	...

The quantum yield has been worked out by assuming that the yellow ceric hydroxide sol absorbed the radiation having average wave-length 436 $\mu\mu$. One such value is worked out below.

K_0 (light & dark) $=0{\cdot}0043$

K_0 (dark) $=0{\cdot}0036$

K_0 for light only $=0{\cdot}0007 \cong 25$ c. mm. of O_2 per hr.

$$=\frac{0{\cdot}025 \times 2 \times 6 \times 10^{23}}{22400 \times 15 \times 60 \times 60} \text{ moles per sec. per c.c.}$$

$$=25 \times 10^{12} \text{ mol. per sec. per c.c.}$$

Magnitude of light absorbed $=0{\cdot}4$ cm. (Moll)

$$=\frac{0{\cdot}4 \times 900}{3{\cdot}8} \text{ ergs, } \left[1 \text{ cm. (Moll)} = \frac{900}{3{\cdot}8} \text{ ergs}\right].$$

No. of quanta absorbed per c. c. per second

$$=\frac{0{\cdot}4 \times 900}{0{\cdot}5 \times 3{\cdot}8} \times 6{\cdot}2 \times 10^{-27} \times \frac{3 \times 10^{10}}{436 \times 10^{-7}}$$

(Thickness of mixture $=0{\cdot}5$ cm.)

$$=4 \times 10^{13}.$$

$$\text{Hence quantum efficiency} = \frac{\text{No. of mol. transformed per sec. per c.c.}}{\text{No. of quanta absorbed per sec. per c.c.}}$$

$$=\frac{25 \times 10^{12}}{4 \times 10^{13}} = 0{\cdot}63 \text{ (approx.)}.$$

Oxidation of glucose in the dark in presence of the same sol has been carried out in the same way. Results are given in Table III.

TABLE III.

Rate of shaking = 60 times per min.

Temp.	O_2 conc.	p_H	Sol conc.	Sugar conc.	$K_0 \times 10^2$.
32°	20%	7·7	0·025*M*	1%	0·0015
,,	,,	,,	,,	2	0·0014
,,	,,	,,	,,	4	0·0015
,,	,,	,,	0·025	1	0·0015
,,	,,	,,	0·016	,,	0·0012
,,	,,	7·7	0·025	,,	0·0015
,,	,,	8·8	,,	,,	0·0025
,,	4%	7·7	,,	,,	0·0015
,,	20%	,,	,,	,,	0·00145
,,	100%	,,	,,	,,	0·0015
32°	20%	,,	,,	,,	0·0015
42°	,,	,,	,,	,,	0·0023

Discussion.

The reaction takes place on the surface of the colloid particles. The rate at which laevulose molecules strike the surface of the colloid is proportional to the free surface.

Rate of deposition $= K_1 S(1-\sigma)$ and the rate at which laevulose molecules leave the surface $= K_2\sigma$, where S = total surface of colloid particles, and σ = portion of the surface covered by the sugar molecules. At equilibrium,

$$K_1 S(1-\sigma) = K_2\sigma$$

$$\text{or,} \quad \sigma = \frac{K_1 S}{K_2 + K_1 S}$$

where K_2 is small compared to $K_1 S$, σ is practically equal to unity, *i.e.*, whole of catalyst is covered by sugar molecules. The reaction velocity which is proportional to surface concentration is given as:

$$\frac{dx}{dt} = K, \quad \text{or,} \quad K = x/t.$$

In other words, velocity will be zero-molecular. In the above experiments K_0 has been calculated in this way and found to be constant.

Absorption of laevulose molecules on the surface of colloid particles is almost instantaneous and the quantity absorbed is independent of the concentration of laevulose even up to very low concentration of laevulose. The value of K_0 has, therefore, been found to be independent of laevulose concentration. But variation in the amount of the catalyst is necessarily associated with variation of total surface and the velocity constant varies accordingly. This is shown in Table IV.

Table IV.

Sol. conc.	Laevulose conc.	$K_0 \times 10^3$.
0·016 *M*	4%	0·0036
,,	1	0·0036
,,	0·33	0·0035
0·009	0·33	0·0027
0·016	,,	0·0035
0·025	,,	0·0039

The surface area S varies as $N \times A$, where N represents the number of colloid particles in the solution and A, surface area of each particle.

If the particles were of same size N would vary as the concentration. Hence K_0 should be proportional to concentration of the sol. The fact, that it is not so, indicates that the sol undergoes dispersion with dilution at constant rate of shaking. Exactly similar relations hold true in the oxidation of glucose in presence of the sol.

It will be noted that the velocity of reaction increases with increase in the rate of shaking which facilitates the interchange of oxygen between the liquid and the gas phase. As is to be expected, increment in the value of p_H also enhances the velocity of catalytic oxidation. The quantum efficiency varies from 0·5 to 1 under the conditions of our experiment.

Oxidation of Sugars by Air in presence of Cerous Hydroxide Gel.

Even at very low concentrations of alkali, glucose and laevulose were found to undergo oxidation by air, in presence of precipitated cerous hydroxide. The oxidations were carried out at p_H, 7·05, 7·09 and 8·6. Phosphate buffers were used in the former two cases and in the last, a suspension of $Mg(OH)_2$ freshly precipitated in a strong solution of $MgCl_2$ acted as a good buffer (Power, *J. Amer. Chem. Soc.*, 1926, **48**, 195). Reaction mixtures were made up as shown here.

Composition of mixtures.	Reaction cell.	Balance cell.
Cerous nitrate solution	5 c.c.	...
NaOH solution	5	...
Sugar solution	5	5 c.c.
Buffer solution	5	5
Water	...	10

The strength of NaOH used was just sufficient to precipitate the cerium completely as hydroxide. The volume of reaction mixture was always 20 c.c. and that of air enclosed in the cell was 132 c.c. nearly. The thickness of the layer of solution inside the cell never exceeded 0·7 cm.

It was, however, found that in absence of catalyst, the laevulose was slightly oxidised by air in phosphate buffers. This slow oxidation of laevulose has always been corrected for in the results presented in the paper. Table V indicates the amount of such oxidation.

TABLE V.

Laevulose = 1%. p_H = 7·8. Temp. = 37·6. Rate of shaking = 60 times per min.

Time.	Manometer reading in Reaction cell.	Balance cell.	Total pressure-drop.
t + 0 min.	0	0	0
t + 240	10	6	4
t + 300	13	9	4
			4 min. = 50 mm. of O_2

It is well known that when a gel of $Ce(OH)_3$ in water is exposed to air, it is slowly oxidised to ceric hydroxide, a pale greenish yellow solid. This ceric compound can be estimated by acidifying the mixture first with HCl and then adding KI followed by subsequent titration of iodine. Further if a warm solution of KI be added first and then the mixture is acidified, the same result is obtained. This fact has been verified experimentally.

When, however, cerous hydroxide undergoes oxidation in presence of sugars, an yellowish brown compound is formed which behaves in a different way from the pale yellow ceric hydroxide. This compound is quite unstable in presence of acids. It was found that if KI be added after acidifying this compound with HCl, practically no iodine is liberated, contrary to the behaviour of ceric hydroxide.

Job (*Ann. chim. phys.*, 1900, **20**, 207) and later on Wieland and co-workers (*Annalen*, 1929, **477**, 32; 1930, **483**, 217) have found that when H_2O_2 is added to a suspension of cerous hydroxide, a brown precipitate of ceric hydroperoxide is formed. In our experiments the brown precipitate obtained during the oxidation of sugars by air in presence of cerous hydroxide, was found to be identical with ceric

hydroperoxide. Ceric hydroxide and ceric hydroperoxide can be readily differentiated by iodine titration. While ceric hydroxide is stable in presence of HCl and can liberate iodine from KI, the ceric hydroperoxide is quite unstable in presence of HCl and can liberate iodine from KI only when KI is added before acidification. That the presence of sugars favours the formation of ceric hydroperoxide instead of ceric hydroxide is clearly proved by the experimental data in Table VI.

TABLE VI.

$Ce(OH)_3$ = 0·0955 g. Temp. = 37·6. p = 7·9 (phosphate).
Rate of shaking = 60 times per min.

Amount of sugar.	Time.	Thio. required when KI is added.	
		Before acidification.	After acidification.
Nil	130 min.	23·5 c.c.	23·3 c.c.
	190	31·0	30·8
0·005 g.	60	17·6	11·4
	300	31·7	21·6
0·05 g.	130	19·6	1·0
	310	21·5	Nil
0·1 g.	190	18·5	Nil

To indicate the procedure of following the relation, a detailed table of results for one experiment is given in Table VII. The summary of results for glucose and laevulose are recorded in Tables VIII and IX respectively. The figures in column 3 stand for total oxygen uptake with correction due to the lapse of 10 minutes between mixing the constituents and closing of manometer stop-cocks. Column 4 denotes the volumes of oxygen used up in the formation of ceric hydroperoxide as estimated iodometrically. K_s represents the constant rate of absorption of oxygen by the system after the first 70 minutes.

TABLE VII.

Glucose = 0·5%. $Ce(OH)_3$ = 0·0478 g. pH = 8·6. Temp. = 37·6.
Rate of shaking = 60 times per minute.

Time. 1	Total pressure drop. 2	Total O_2, uptake with corr. 3	O_2 uptake by $Ce(OH)_3$ to form hydroxide. 4	O_2 for glucose. 5	Ks. 6
10 min.	0	0 c. mm.	0 mm.	...	...
70	76	1153	1071	82 c.mm.	0·0405
130	91	1348	1120	228	—
190	106	1543	1167	376	0·0407
250	119	1712	1197	515	0·0403
310	130	1855	...	...	...
					0·0405

TABLE VIII.

Oxidation of glucose.

Rate of shaking per min.	Temp.	O_2-conc.	pH.	Amt. of $Ce(OH)_3$.	Conc. of glucose.	Total O_2 uptake at 70 min.	Total O_2 uptake at 250 min.	O_2—$Ce(OH)_3$ at 70 min.	O_2—$Ce(OH)_3$ at 250 min.	Ks.
60	37·6°	20%	8·6	0·0478g.	1%	1062	1687	961	1081	0·0469
,,	,,	,,	,,	,,	0·5	1153	1712	1071	1197	0·0405
,,	,,	,,	,,	,,	0·25	1168	1753	1997	1298	0·0351
,,	,,	,,	7·9	0·0239	0·25	137	384	127	148	0·0206
,,	,,	,,	,,	0·0478	,,	394	914	337	489	0·0344
,,	,,	,,	,,	0·0955	,,	1198	2186	1054	1460	0·0531
,,	,,	,,	7·05	0·0478	,,	349	739	280	371	0·0281
,,	,,	,,	7·9	,,	,,	394	914	337	489	0·0344
,,	,,	,,	8·6	,,	,,	1168	1753	1097	1298	0·0351
,,	,,	100	7·9	0·0955	,,	1774	2801	1620	2058	0·0536
,,	,,	60	,,	,,	,,	1380	2420	...	1740	0·0540
,,	,,	,,	,,	,,	,,	1198	2186	1054	1460	0·0531
,,	,,	20	,,	,,	,,	1198	2186	1054	1460	0·0531
,,	27·6°	,,	,,	,,	,,	910	1599	874	1348	0·0200
60	37·6°	,,	,,	,,	,,	1198	2186	1054	1460	0·0531
30	,,	,,	,,	,,	,,	923	...	878	...	0·0406

TABLE IX.

Oxidation of laevulose.

Rate of shaking per min.	Temp.	Conc. of O_2.	pH.	Amount of $Ce(OH)_3$.	Conc. of laevulose.	Total O_2 uptake at 2 hrs.	$O_2 \equiv Ce(OH)_3$ at 2 hrs.	K_S (after 2 hrs.),
60 times	37·6°	20%	7·05	0·0955 g.	0·5%	1963	776	0·0552
,,	,,	,,	,,	,,	0·25	2110	972	0·0446
,,	,,	,,	,,	,,	0·125	1716	1107	0·0329
,,	,,	,,	,,	0·0955	0·25	2110	972	0·0446
,,	,,	,,	,,	0·0477	,,	797	304	0·0375
,,	,,	,,	,,	0·0238	,,	412	147	0·0306
,,	,,	,,	7·05	0·0955	,,	2110	972	0·0446
,,	,,	,,	7·9	,,	,,	2782	1038	0·0570
,,	,,	,,	8·6	,,	,,	3029	1263	0·0561
,,	,,	,,	7·05	0·0477	,,	797	304	0·0375
,,	,,	60	,,	,,	,,	819	317	0·0364
,,	,,	100	,,	,,	,,	832	324	0·0368
,,	47·6	20	,,	,,	,,	1023	351	0·0685
,,	37·6	,,	,,	,,	,,	797	304	0·0375
,,	,,	,,	,,	,,	,,	797	304	0·0375
30 times	,,	,,	,,	,,	,,	689	284	0·0270

In presence of visible radiations, the rate of absorption of oxygen increased some what, as shown in Table X.

TABLE X.

Temp. = 37·6°. Conc. of sugar = 0·25%. Conc. of O_2 = 20%. $Ce(OH)_3$ = 0·0478 g.

Sugar.	Rate of shaking per min.	p_H.	K_S(dark).	K_S (dark and light.)
Glucose	30 times	7·9	0·0406	0·0487
Laevulose	60 times	7·05	0·0365	0·0420

Inhibition by glycine.—Dhar and collaborators (*J. Phys. Chem.*, 1930, **34**, 711) have shown that glycine is oxidised by air in presence of cerous hydroxide. But it was found in course of experiment that at a p_H as low as 7·9, glycine is quite indifferent to air in presence of $Ce(OH)_3$, at 32°. One such experiment is given below.

TABLE XI.

Temp = 32°. p_H = 7·9. t = 120 minutes.

Conc. of glycine.	Amount of $Ce(OH)_3$.	Total O_2 absorbed.	O_2 taken by $Ce(OH)_3$.	O_2 taken by glycine.
1%	0·0478 g.	158	153	5 c. mm.
1	0·0478	160	154	6

Use of glycocoll buffers for the reactions was hence attempted. It was, however, found that oxidation of glucose is strongly retarded as shown in Table XII.

TABLE XII.

Conc. of glucose = 0·25%. Temp. = 37·6°. Amount of $Ce(OH)_3$ = 0·0478 g. Rate of shaking = 60 times per min.

Quantity of glycine.	p_H.	K_S.
Nil	7·9	0·0344
0·02 g.	8·0	0·0297

The yellow compound formed from $Ce(OH)_3$ was estimated in two ways by acidifying the mixture before and after addition of KI. The analysis of ceric compounds are given in Table XIII.

TABLE XIII.

Glycine=0·02 g. Glucose=0·25%. p_H=8·0. Ce $(OH)_3$=0·0478 g.

Rate of Shaking =60 times per min.

	Thio. required when KI is added	
Time.	After acidification.	Before acidification.
70 min.	3·0 c.c.	3·2 c.c.
130	3·0	3·2
190	3·0	3·2

It may therefore be concluded that in presence of glycine practically $Ce(OH)_3$ is formed and no ceric hydroperoxide can be detected.

DISCUSSION.

The oxidation of organic substances by oxygen with the aid of enzymes or inorganic catalysts has been pictured by Wieland as consisting of a preliminary process of dehydrogenation followed by the formation of hydrogen peroxide; and in some recent work of his school, cerous hydroxide in small quantities has been used for detecting the formation of hydrogen peroxide during the processes of enzymic oxidation.

In the experiments recorded above, cerous hydroxide not only serves as a detector for hydrogen peroxide produced during the course of ærobic oxidation, but its particles provided an active surface for the dehydrogenation of the sugars preliminary to the actual combination of the liberated H_2 with O_2 to form hydrogen peroxide. Similar properties are exhibited by oxidised platinum atoms present on the surface of platinum black catalysts.

Willstätter and Waldschmidt Leitz (*Ber.*, 1921, **54**, 119) maintain that "dass oxydiertes Platin und Palladium den Wasserstoff, den sie aufnehmen, in leichter dissozierbarer Bindung, in reactionfahiger form, enthalten als Palladium und Platinhydrur." We may postulate that the chemical reaction can be represented by the following equations where SH_2 stands for the substrate sugar molecule.

$$SH_2 + Ce(OH)_3 \rightleftharpoons S + \begin{matrix} H \\ H \end{matrix}\!\!>\!Ce(OH)_3 ; \; S + H_2O \rightarrow SHOH \quad \ldots \quad (i)$$

$$\begin{matrix} H \\ H \end{matrix}\!\!>\!Ce(OH)_3 + O_2 \rightleftharpoons Ce(OH)_3 + H_2O_2 \quad \ldots \quad \ldots \quad (ii)$$

$$2\,Ce(OH)_3 + 3\,H_2O_2 \rightleftharpoons 2Ce(OH)_3 - OOH + 2\,H_2O \quad \ldots \quad (iii)$$

$$4\,Ce(OH)_3 - OOH \rightleftharpoons 4Ce(OH)_3 + 2\,H_2O + 3O_2 \quad \ldots \quad (iv)$$

At the beginning of the reaction, the entire catalytic surface is made of cerous hydroxide, and reactions (*i*) and (*ii*) proceed at a rapid rate. The nature of the catalytic surfaces changes as more and more of cerous hydroxide is converted into ceric hydroperoxide which is not capable of effecting the priliminary dehydrogenation of the substrate. After about an hour the reactions (*iii*) and (*iv*) balance each other, and the relative surface area of cerous hydroxide to ceric hydroperoxide attains practically constant values. Thereafter we meet with a steady rate for the absorption of oxygen which is the difference between the rate of absorption of oxygen to form hydrogen peroxide and the rate of decomposition of ceric hydroperoxide. Table VII shows that the amount of ceric hydroperoxide present in the catalytic system attains 90% of its equilibrium value in 70 minutes and full equilibrium value in about 300 minutes. The rate of absorption of oxygen when this stationary condition is practically reached is given in last columns of tables VII, VIII, IX.

It is clear from table XII that glycine is a powerful inhibitor of the preliminary dehydrogenation by the cerous hydroxide catalyst and the subsequent formation of peroxide. Dhar has always emphasised the point of view that the oxidation of carbohydrates is retarded by the presence of fats and protiens. Willstire (*Z. Physiol.*, 1931, **72**, 88) has recently shown that the enzymic oxidation of adrenaline is very considerably delayed by the presence of amino-acids. Our investigation furnishes another illustration of the inhibition by amino-acids of the ærobic oxidation of sugars by inorganic catalysts.

The slightly catalytic action of illumination on ærobic oxidation in the present case is to be ascribed to the probable enhancement in the velocity of reaction (*iv*). This would ensure a larger relative ratio of the surface of cerous hydroxide to that of ceric hydroperoxide. Experiments to test this hypothesis are in progress.

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Effect of Temperature on Selective Adsorption by Silica Gel from Binary Mixtures.

By M. R. Aswathanarayana Rao.

Selective adsorption from binary mixtures has been investigated by a number of workers (Williams, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, No. 23; Ostwald and Izaguirre, *Kolloid Z*, 1922, **30**, 279; Jones and Outridge, *J. Chem. Soc.*, 1930, 1574; Bartell and Scheffler, *J. Amer. Chem. Soc.*, 1931, **53**, 2507; Rao, *J. Phys. Chem.* 1932, **36**, 615). There is no published work, however, on the effect of temperature on selective adsorption. Investigations on the effect of temperature on selectivity are described in the present paper. The term selectivity is given by the equation,

$$S = m\,(C_1 - C_2)/g$$

where S denotes selectivity (apparent adsorption); m, weight of the liquid mixture added to the gel; g, weight of the gel in equilibrium with the liquid ; C_1, the initial concentration of the selectively adsorbed component; C_2, the equlibrium concentration of the same component, C_1 and C_2 being expressed in weight fraction.

Mixtures which have the **U** and **S**-shaped curves (when selectivity is plotted against C_2) were used to study the variation of selectivity with temperature. For **U**-shaped curves binary mixtures of benzene with (*a*) alcohol, and (*b*) heptane were used. For the **S**-shaped curves mixtures of pyridine and water were employed.

Experimental.

The organic liquids were purified by the usual methods employed in organic chemistry. The purity was further tested by finding out the refractive indices before and after shaking them with the gel. It was found that there was no change. The gel used was prepared in this laboratory by the method of McGavack and Patrick (*J. Amer. Chem. Soc.*, 1920, **42**, 951). The moisture content was 3·36 % and the gel adsorbed 0·362 c.c. of benzene from the saturated vapour.

FIG. 1.

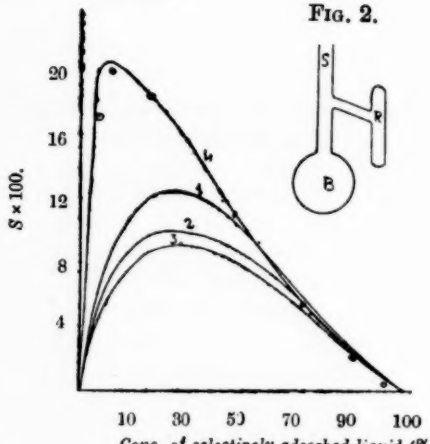


FIG. 2.

Curves 1-3 represent benzene-heptane at 30°, 74° and 98° respectively and curve 4 for benzene-alcohol at 30°.

⊙ ⊙ ⊙ points for S at 63°.

. . . „ „ at 98°.

Figure 2 shows the type of vessel used to carry out the selective adsorption measurements. The side reservoir R, served to transfer the liquid from the bulb B when the equilibrium was attained. The dry vessel was weighed before and after the introduction of the activated gel. After cooling the bulb in ice for some time, the mixture was introduced into it by means of a narrow funnel whose lower end was about one cm. above the level of the gel in the bulb. This prevented the liquid sticking to the sides of the vessel. Care was taken to see that neither the gel nor the liquid entered the reservoir. The bulb was weighed and sealed off at S, and kept vertically in a water thermostant for 30 hours to attain equilibrium. The liquid did not condense in the reservoir at the end of this period. The vessel was then tilted and the equilibrium mixture separated from the gel by allowing the liquid to flow into R. It was then taken out of the thermostat and allowed to cool. The side tube was cut off, and the composition of the liquid in the reservoir was found using a Pulfrich Refractometer. A blank experiment showed that there was no change in concentration when two solutions (of different concentrations) were placed one in the reservoir and the other in the bulb and heated to 97° for half an hour. The following results were obtained.

TABLE I.

Mixture used = benzene and heptane. Selectively adsorbed component = benzene. C'_2 = % wt. of benzene in the equilibrium mixture.

30°		74°		98°	
C'_2.	$S \times 100$.	C'_2.	$S \times 100$.	C'_2.	$S \times 100$.
2·0	4·30	8·4	7·03	9·0	6·42
...	...	...	...	18·2	8·50
4·8	6·56	28·0	9·61	29·2	9·10
7·0	7·96	37·9	9·86	47·3	8·34
10·0	9·72	46·4	8·86	60·1	7·17
19·5	11·65	60·9	7·24	70·6	5·33
41·8	11·53	70·6	5·75	79·8	3·45
64·4	7·19	91·2	0·82	90·8	0·67
80·4	4·56	...	...	...	...
94·3	1·06	...	...	...	...

TABLE II.

Mixture used = benzene and alcohol. Selectively adsorbed component = alcohol. C'_2 = % wt. of alcohol in the equilibrium mixture.

30°		63°		98°	
C'_2.	$S \times 100$.	C'_2.	$S \times 100$.	C'_2.	$S \times 100$.
0·4	12·80	1·6	11·77	19·5	17·80
2·6	19·00	3·0	17·34	42·65	12·25
6·1	20·84	6·3	20 72	54·4	9·39
11·0	20·20	18·8	18·80	68·9	5·18
18·4	18·90	53·1	9·56	84·3	2·56
42·6	12·06	68·2	5·38	94·1	0·74
68 6	5·36	84 7	2·29	...	...
81·6	2·27	94·0	0·81	...	...
24·1	0·32	...	...	...	...

TABLE III.

Mixture used = pyridine and water. C'_2 = % weight of pyridine in the equilibrium mixture.

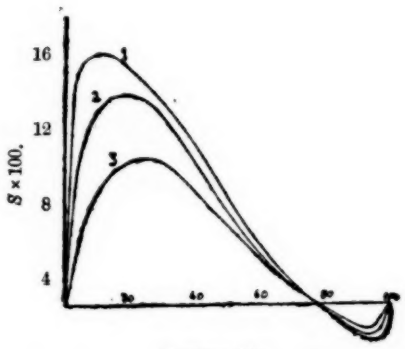
30°		74°		98°	
C'_2.	$S \times 100$.	C'_2.	$S \times 100$.	C'_2.	$S \times 100$.
4·2	11·7	5·8	8·17	7·2	5·57
11·6	15·30	12·6	12·57	15·4	8·07
27·4	13·22	20·9	12·01	30·9	8·66
46·2	7·94	45·2	7·97	46·7	5·56
63·1	3·03	62·6	3 33	63·6	1·59
77·5	0·26	77·4	0·38	81·7	−0·21
81·7	−0·40	84·9	−0·44	85·1	−0·86
85·2	−1·03	90·7	−1·67	90 5	−1·21
90·8	−1·94	95·6	−1·87	95·6	−1·75
95·8	−2·23	98·5	−1·59	98·4	−1·31
98·6	−1·90	...	...	...	...

DISCUSSION.

It is clear from Figs. 1 and 3 that as the temperature increases, the selectivity decreases. The decrease depends upon the particular mixture used. Thus in the case of alcohol-benzene mixtures, the points obtained for selectivity at higher temperatures lie so close to the curve at 30° that no attempt is made to draw the curve through these points. It is also evident that the decrease in selectivity does not depend upon the magnitude of selectivity although the maximum values at various temperatures occur at almost the same equilibrium concentration. Thus in the case of benzene-alcohol mixtures, the maximum for selectivity at 33° is 0·208 while the difference in selectivity values at 30° and 60° is only 0·006. In the case of benzene-heptane mixtures, the maximum selectivity is 0·117 but the difference between the two selectivity values is about 0·02 for the same two temperatures and at the same equilibrium concentration of 6% benzene by weight. The maximum value of selectivity occurs at about 38% benzene-heptane

mixtures for all temperatures. In the case of alcohol-benzene mixtures this value occurs at 6% alcohol concentration.

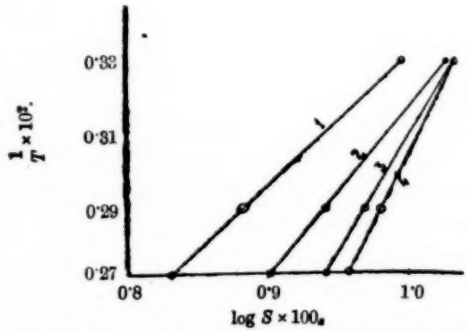
FIG. 3.



Pyridine (%).

1-3 represent $S - C_2$ curves at 30°, 74° and 98° respectively.

FIG. 4.



1-4 represents log S-$1/T$ curves when C_2 equals 0·10, 0·15, 0·20 and 0·25 respectively.

Figure 3 represents the S-shaped curve obtained with pyridine-water mixtures. The remarks made in the previous paragraph apply to this also. It is of interest to know whether the point of zero selectivity

(at about 78·6 % of pyridine) remains at the same equilibrium concentration at all temperatures. In the experiments that were tried it was found that this point was almost identical. Thus at 30° the zero selectivity occurred at 78·45 % pyridine concentration whereas at 98° it occurred at 78·0 %.

A relationship can be deduced between selectivity and the amount of selectively adsorbed liquid by taking benzene-alcohol mixture into consideration. It has already been pointed out that alcohol is selectively adsorbed at all concentrations. Let m/g in the selectivity formula (formula I) be designated M. When equilibrium has attained, let C_g be the concentration of alcohol (in weight fraction) in the liquid adsorbed by the gel and let m' be the weight of the mixture adsorbed by 1 g. of the gel. It is clear that

$$M(C_1)=(M-m')\,C_2+m'C_g$$

$$\text{or}\quad M(C_1-C_2)=m'\,(C_g-C_2)=\text{Selectivity.} \quad \ldots \qquad \ldots \quad (ii)$$

Thus selectivity represents the excess of alcohol adsorbed by 1 g. of the gel (owing to the selective nature of adsorption) over what would have been present if there were no preferential adsorption. Hence for an increase in selectivity at the same equilibrium concentration C_2, either m' or C_g should increase. But the increase in m' is comparatively small and hence C_g must increase for an increase in selectivity.

It is usually assumed that the surface of the gel is responsible for the greater adsorption of alcohol (Jones and Outridge, *loc. cit.*). It has also been shown that selectivity is a single-valued function of the equilibrium concentration whether the experiment is done in the vapour phase or in the liquid phase. The mechanism of selective adsorption of alcohol on silica gel from a binary mixture of alcohol and benzene is analogous to that of the adsorption of a single gas or vapour and the formula derived for the latter phenomenon is applied to the selective adsorption of alcohol.

According to Williams (*Proc. Roy. Soc.*, 1919, **A**, **96**, 287, 298)

$$\log \frac{x}{C}=K_1+K_2/T$$

where x denotes amount of the gas (in moles) adsorbed per unit weight of the solid; $C=1/V$, the conc. of the gas ; T, absolute temperature ; K_1 and K_2 being constants.

Henry (*Phil. Mag.*, 1922, **44**, 68) arrived at an identical formula from entirely different assumptions based on the reasoning of Langmuir. Applying this equation we get

$$x = C \cdot e^{k_1 + \frac{k_2}{T}}$$

where x = amount of alcohol in moles adsorbed per unit weight of the gel; $C = C_2$, the equilibrium conc. K_1 and K_2 are constants.

Combining this with Eq. (*ii*) we get

$$S = m'C_g - m'C_2 = KC_2.e^{k_1 + \frac{k_2}{T}} - m'C_2 \text{ (where } K \text{ is a constant).}$$

$$= C_2\left(Ke^{k_1 + \frac{k_2}{T}} - m'\right) \qquad \ldots \quad (iii)$$

The above equation indicates that selectivity decreases with rise in temperature. This equation, it must be noted, applies to dilute solutions only.

In the equation (*iii*) if C_2 is constant, the variation of m' with temperature is comparatively small; since the volume of the liquid adsorbed by a porous substance is fairly constant at all temperatures (*cf.* McBain, "Sorption of Gases and Vapours", p. 486). Hence when C_2 is small, a straight line should be obtained when log S is plotted against $1/T$. The following values are obtained from the benzene-heptane curves at different temperatures. S_1, S_2 and S_3 are the selectivity values at 30°, 74° and 98° respectively.

TABLE IV.

$C_2 \times 100$.	log $S_1 \times 100$.	log $S_2 \times 100$.	log $S_3 \times 100$.
10	0·8325	0·8774	0·9823
20	0·9030	0·9415	10414 1·0414
20	0·9405	0·9694	1·0682
25	0·9562	0·9814	1·0930

$\frac{1}{T_1} = 0{\cdot}3301 \times 10^{-2}$, $\frac{1}{T_2} = 0{\cdot}2882 \times 10^{-2}$, $\frac{1}{T_3} = 3{\cdot}2699 \times 10^{-3}$.

In Fig 4, the values of S_1, S_2 and S_3 are plotted against $1/T_1$, $1/T_2$ and $1/T_3$ respectively. Straight lines are got in every case as predicted by the equation (*iii*).

Equation (*iii*) has been derived for a **U**-shaped curve. The **S**-shaped curve can be considered as being made up of two **U**-shaped curves each representing the selectivity of one of the components. The same equation can therefore be applied in explaining the decrease in selectivity with rise in temperatnre.

Summary.

1. The variation of selective adsorption with temperature has been measured using silica gel with the following mixtures:—(*i*) benzene-heptane, (*ii*) alcohol-benzene, and (*iii*) pyridine-water, over entire range of concentrations.

2. It has been found that the selectivity decreases with a rise in temperature.

3. An equation has been derived to explain the observed changes in selectivity.

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Effect of Ultraviolet Light on Enzymatic Reactions. Part I. Diastase.

By Sobhanlal Banerjee and H. K. Sen.

While studying the decomposition of α-keto-carboxylic acids by organic catalysts, it was noticed that in certain instances when the decomposition was effected in the presence of ultraviolet light, the catalysts suffered a perceptible diminution in their activity. Thus in the presence of ultraviolet light, gelatine, egg-albumin, and urea suffered diminution in their catalytic power of decomposing pyruvic acid, whereas catalysts like phenylaminoacetic acid, asparagine, activated charcoal, platinum, etc., retained their usual activity. If natural enzymes be provisionally regarded as highly complex bodies, nitrogenous or otherwise, it may be inferred similarly that the ultraviolet light would cause a destruction or retrogression of their usual activity. This is usually the case. There appeared, however, the possibility of stopping such destruction by the use of accelerators, the assumption being that the rate of inhibition by the ultraviolet falls short of the rate of acceleration by the accelerators. Viewed differently, the accelerators may in fact serve as filters against the ultraviolet. Although, separately, an accelerator solution may act as a filter, in a solution with the substrate and the enzyme, the reaction of the ultraviolet may be considered more of a selective nature, the accelerators being more sensitive to the light thrust. With phenylaminoacetic acid, etc., the activation of the carboxylase reaction of yeast is definite, and a further attempt was made to increase the catalytic action by ultraviolet light treatment. The result was destructive. With diastase, however, the result was different. Ordinarily, the diastatic ferment in malt is known to be completely rendered inactive by the ultraviolet light (*cf.* Pincussen, *Biochem. Z.*, 1923, **134**, 459; 1924, **144**, 366; 1924, **152**, 406, 416). The protective action of some salts, with special reference to the degree of protection rendered by particular kations, was also investigated by his school (Pincussen and Kumanomidoh, *Biochem. Z.*, 1928, **195**, 79). Thus, potassium chloride offers less protection than magnesium chloride,

which again was less effective than calcium chloride. The explanation suggested by him relates to the probable coarsening of the enzyme particles by the action of the ultraviolet light. This analogy is derived from the known capacity of such light to effect a coarsening in the colloidal system. Considering the enzyme as a dual complex between a colloidal member and another active portion, the *acceptor*, adsorbed on the colloid, a change in the dispersion of the colloid of the enzyme by the action of the ultraviolet light would, in all probability, inhibit its activity. In fact, a retardation in the velocity of enzyme action does take place. The addition of salts would also cause a change in the dispersion grade of the enzyme, but if this change is such that the light cannot affect the enzyme any more then a certain amount of protection would be exercised by the salt. It is further known that potassium salts change the dispersion less than calcium, *i.e.*, the dispersed particles are rendered coarser by the latter, and hence less susceptible to the action of light. From the experimental data of Pincussen, this protection by salts appears to be of a very moderate order, but in our case, with phenylaminoacetic acid, etc., the protection is substantially marked. It is not known that these amino acids have any action similar to those of salts. It seems, therefore, that amino acids act as protective agents for different reasons, which may be provisionally regarded as of the nature of a light screen. We could not confirm Pincussen's statement in this connection that the activity of an enzyme can be revived if a minute amount of fresh enzyme is added to the illuminated system (*Fermentforschung*, 1925, **8**, 181). Nor can we at this stage definitely state that purified enzymes are most sensitive to the action of light (*loc. cit.*). In the present case, purified malt diastase was used, whilst in Pincussen's experiments, pancreatic diastase was taken for this portion of the work. Mention may further be made of the protective action of dyestuff (Claus, *Biochem. Z.*, 1929, **204**, 456 ; Pincussen and Kambayashi, *ibid.*, 1928, **203**, 334), but it has no particular bearing on our present work. It was observed in course of this work that the several amines, amino acids and ammonium salts etc., not only increase the activity of the diastase itself, but also protect the enzyme from complete destruction by the action of the ultraviolet rays, the activity of the enzyme, however, being appreciably minimised. Such destructive property of the ultraviolet light in therapy is very significant, but the discovery of protective reagents would be no less

important, as the latter would no doubt increase the flexibility in the employment of such light in actino-therapeutic science. Accordingly, four sets of experiments were performed with malt diastase: (*i*) without catalyst, (*ii*) with catalyst, (*iii*) with catalyst and ultraviolet light, (*iv*) without catalyst and with ultraviolet light. The following table gives the results of such experiments. It will be noticed that the diastatic values given under column 3, are not the same. The reason for this is the difference in strength of the diastase solution which was freshly prepared for each set of experiments.

TABLE I.

1 C.c. of 0·1% soln. of catalyst used.

Catalyst.	Control expt. Diastatic value. D_1	With catalyst. Diastatic value. D_2	With catalyst & ultraviolet. Diastatic value. D_3	Control expt. Without catalyst with ultraviolet. Diastatic value. D_4	Constant p^H value.
Asparagine	18·5	31·8	Nil (15 mins.)	Nil (45 mins.)	5·6
Phenylaminoacetic acid	31·8	48·5	8·5 ,,	Nil ,,	5·6
Asparagine	23·5	31·8	9·6 (5 mins.)	Nil	5·6
Gelatine	23·5	23·5	15·16 ,,	Nil (5 mins.)	5·4
Gelatine	31·8	31·8	9·6 (45 mins.)	Nil (45 mins.)	5·6
Egg-albumin	31·8	31·8	Nil ,,	Nil ,,	5·6
Glutamic acid	31·8	31·8	Nil ,,	Nil ,,	5·4
Leucine	23·5	23·5	Nil ,,	Nil ,,	5·4
Tyrosine	48·5	48·5	9·6 ,,	Nil ,,	5·4
Aminobenzoic acid	23·5	31·8	9·6 ,,	Nil ,,	5·6
Ammonium tartrate	23·5	31·8	Nil ,,	Nil ,,	5·4
Ammonium oxalate	18·5	23·5	Nil ,,	Nil ,,	5·6
Ammonium benzoate	31·8	31·8	Nil ,,	Nil ,,	5·6
Ammonium formate	18·5	18·5	Nil (45 mins.)	Nili (45 mins.)	5·6
Ammonium citrate	23·5	31·8	Do	Do	5·8
Do	23·5	31·8	Nil (10 mins.)	Nil (10 mins.)	5·6
Do	18·5	23·5	11 (5)		5·6
Ammonium chloride	23·5	23·5	Nil (10)	Nil (10 mins.)	5·4
Ammonium bromide	18·5	18·5	Do	Do	5·4
Microcosmic salt	23·5	23·5	Do	Do	5·6
Urea	23·5	23·5	Nil (45 mins.)	Nil (45 mins.)	5·6
Phenylurea	31·8	31·8	Do	Do	5·6
Thiourea	23·5	23·5	Do	Do	5·6

It would appear from the previous table that asparagine, phenylaminoacetic acid, ammonium citrate, gelatine, tyrosine, aminobenzoic acid etc., cause varying degrees of increment of diastatic activity and exert protective action on malt diastase against the ultraviolet light. Thus, an exposure of 5 minutes to the ultraviolet light (3000 C. P., 12" arc) at a distance of 2′ was just sufficient to completely destroy the diastatic activity of a sample of malt. If gelatine was added during the reaction, and the whole was exposed to the ultraviolet for 5 minutes only as in the previous case, the diastatic power, though reduced, was still found to be 15·16—and when exposed for 45 minutes the diastatic value was 9·6. On the other hand, for the same period of 5 minutes, ammonium citrate under identical conditions, gives the diastatic value 11. This shows that the protective action of gelatine is greater than that of ammonium citrate. It is obvious that a distinction must be drawn between an accelerator and a protector. But it is quite possible that certain substances function as both. For example, phenylaminoacetic acid, tyrosin, aminobenzoic acid, ammonium citrate are both accelerators and protectors. Whilst from the chemical nature of the accelerators, a surmise may be drawn as to the nature of the diastatic fraction of the malt, the protective action probably depends upon the capacity to absorb partially or wholly the destructive wave-lengths of the ultraviolet light. Expressed in a slightly different way, the light acts selectively on these protectors leaving the diastatic enzyme wholly or partially active. This appears plausible when we consider that gelatine, ammonium citrate and, in fact, many albuminoid substances are affected by the ultraviolet light.

Procedure.—The diastase used in the present investigation was prepared in the usual way, by steeping barley in water and then allowing the grains to germinate in a warm place until the plumules were 1/2 inch in length. The dry malt was then extracted with two to four parts of 20% alcohol for 24 hours. The solution was filtered and precipitated with 2 to 2·5 parts of absolute alcohol, treated with ether and dried in *vacuo*. The preparation was redissolved in water, then reprecipitated and dialysed. In these experiments, 0·15 to 0·2 g. of the dry diastase was dissolved in 100 c. c. of water and filtered before use.

The diastatic value was determined by the Lintner method. In each of a series of ten clean and numbered test tubes of approximately the same bore, is placed the same quantity of soluble starch solution

(usually 10 c.c. of 2% soln.) and then a progressively increasing quantity of the diastase extract, *i.e.*, 0·1 c.c. in No. 1 tube, 0·2 c.c. in No. 2, 0·3 c.c. in No. 3 and so on. The contents are mixed and placed in a bath kept constant near about the room temperature for exactly one hour 5 C.c. of Fehling's solution are now added in each tube as quickly as possible and the tubes are now heated in a boiling water-bath for 20 minutes and then examined. Some of the tubes in the series will show no blue colour, or are faintly yellow, whilst others are still blue. The amount of enzyme in the first colourless tube is that amount which will just convert the fixed amount of starch into maltose in the given time.

The diastatic power is based upon 0·1 c.c. of the enzyme solution and called 100.

Therefore, if the result was between the 6th and 7th tube, the diastatic power $D = \frac{100 \times 0{\cdot}1}{0{\cdot}65} = 15{\cdot}4$.

Before adding the enzyme into starch solution, the p_H of the latter was determined colorimetrically, with and without the solution of the so-called activator. The p_H of the solutions was kept always constant (for the same set of experiments) either by the addition of $N/100$-NaOH or $N/100$-HCl to the starch solution in which the solution of the catalyst has been added and making neutral to Wisslow's indicator (mixture of methyl red and methyl blue). This was necessary to show that the effect of the activators is not due to a more favourable hydrogen ion concentration induced by their presence (amino acids etc. *cf.* Sherman and Thomas, *J. Amer Chem. Soc.*, 1923, **45**, 1960; 1921, **43**, 2461). The catalyst added was usually 1 c.c. of its 0·1 % solution.

The experiments with ultraviolet light were carried out in quartz tubes. The mercury vapour lamp used was of 3000 C. P.—with an arc of 12″ and it was placed at a distance of two feet from the tubes meant for exposure.

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Chemical Examination of *Cuscuta Reflexa*, Roxb. Part I. The Constituents.

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Cuscuta reflexa (Roxb.) known as Amarvel or Akashbel in Hindusthani and Swarnalata in Bengali, is a common golden yellow dodder like parasite belonging to the Natural Order *Convolvulaceae*. It is common throughout India growing on thorny or other shrubs.

As regards its medicinal properties Mahommedan writers consider it to be alterative and depurative, a purge for bile and black bile, useful in affections of the brain such as fits, melancholy, insanity, etc. (Dymock, "Pharmacographica Indica," 1890, Vol. II, 548). It is also supposed to be purgative and used externally against itch, and internally in protracted fevers, retention of wind, and induration of the liver (Kirtikar and Basu, "Indian Medicinal Plants," 1918, Vol. II, 888).

Very little is known regarding the chemical composition of *Cuscuta reflexa*, though Barbey in 1895 (*J. Pharm.*, 1895, *vi*, 2, 107) working on another variety of cuscuta, namely, *C. epithymum*, isolated from it an yellow amorphous colouring matter by precipitation of an alkaline extract with dilute sulphuric acid and subsequent extraction of the precipitate with ether. He termed the colouring principle cuscutin but gave no analytical data. He also isolated along with tannins and resinous substances a small amount of a crystalline substance having a faint odour of coumarin.

On account of the medicinal properties associated with *Cuscuta reflexa* in India the present authors were tempted to put it to a more systematic chemical analysis. We have been able to isolate cuscutin, the colouring matter of Barbey (*loc. cit.*), in a crystalline form (0·2 %) along with a white crystalline substance having the properties of a lactone, called by us cuscutalin (1·0 %), a small amount of brown wax (0·1 %) and large quantities of reducing sugars.

For the isolation of cuscutin we tried at first the method adopted by Barbey, but the colouring matter obtained was non-fusible and could not be made to crystallise. We, therefore, worked with sun-dried material and got the colouring matter in a crystalline form from the aqueous solution of the alcoholic extract after the removal of cuscutalin.

Cuscutin is feebly acidic in properties since it dissolves in sodium bicarbonate solution with slight effervescence and can be precipitated

unchanged by acids. It forms a diacetyl, a dicarbethoxy and a dimethoxy derivative and gives a very delicate violet green colour with ferric chloride; hence it contains two phenolic hydroxy groups. It does not form any oxime.

Cuscutalin is a lactone. It dissolves in caustic alkalis with a yellow colour. Although containing no aldehydic or ketonic group it reduces Tollen's reagent slowly and gives a reddish brown colouration with an alkaline solution of potassium nitroprusside. These reactions definitely prove it to be a member of the $\triangle a\beta$-lactones, which have been adequately reviewed by Jacobs (*J. Biol. Chem.*, 1926, **67**, 333; *Phys. Rev.*, 1933, **13**, 222). More work on the elucidation of its constitution is in progress.

Pharmacologically cuscutalin appears to be a potent drug. It has been sent to King George's Medical College, Lucknow, where a detailed study of its physiological properties will be undertaken.

Experimental.

30 Kg. of the fresh *Cuscuta reflexa* were collected from the neighbourhood of Allahabad in the months of October and November from various host plants. A preliminary examination showed that the chemical composition of the parasitic plant was practically independent of the nature of its host. It was dried in the sun and by so doing lost about 90% of its moisture. It was then finely crushed and when burnt in a porcelain dish left 9·85 % of a brownish white ash. This ash consisted of 19·12 % of water-insoluble and 80·88 % of water-soluble inorganic material. The following elements and radicals were detected in the ash: Sodium, potassium, magnesium (traces), calcium, nitrates, phosphates, carbonates and silica.

Samples of the finely crushed material were extracted in a Soxhlet's apparatus using various solvents when the following amounts of extracts dried at 100°, were obtained.

Petroleum ether extract.—The extract was of a deep green colour, containing a greenish white crystalline matter suspended in it, yield 15·2%.

Chloroform extract.—The extract was of a pale yellow colour and contained a small amount of a pale yellow deposit, yield 18·0%.

Alcoholic extract.—The colour of the extract was greenish yellow containing a large amount of crystalline matter, yield 22·5%. It

reduced Fehling's solution easily. It gave a lead salt with neutral lead acetate, a silver salt with silver nitrate, deep greenish blue colour with ferric chloride. No reactions for alkaloids were obtained.

Aqueous extract.—The extract was of a light orange colour, reduced Fehling's solution readily and gave a deep green colour with ferric chloride, yield 5·0 %.

The powdered material (2·5 kg.) was extracted with boiling alcohol in a big extraction flask of 5 litre capacity, till the extract failed to give any white stuff on cooling. The extract, which was of a light yellow colour, was filtered hot and on cooling deposited cuscutalin which was filtered, washed with cold alcohol till a perfectly white stuff was obtained. In order to remove the whole of the crystalline matter from the plant at least five extractions are necessary. It was dried in *vacuuo* over calcium chloride and weighed 25 g., m.p. 64°. It was recrystallised from methyl alcohol, when a yellowish brown substance was left which would not go into solution even on prolonged boiling and melted at 74°. From its properties it appears to be a wax. The quantity obtained was too small for any detailed investigation. Cuscutalin was finally recrystallised from a large volume of boiling ethyl alcohol, when perfectly white crystalline flakes were obtained, m.p. 68°.

Properties of cuscutalin.—Cuscutalin is a colourless crystalline substance, insoluble in water, soluble in benzene, phenol, chloroform, ether and slightly so in ethyl alcohol, methyl alcohol, ethyl acetate, pyridine and acetic acid. It dissolves in boiling caustic potash or caustic soda solution giving a beautiful yellow colouration. It decolourises a solution of bromine in chloroform and a dilute alkaline solution of potassium permanganate. It gives a positive Salkowski's reaction, *i.e.*, a solution of cuscutalin in chloroform and concentrated sulphuric acid gives a red and finally a green colouration. If cuscutalin is dissolved in chloroform and a little acetic anhydride is added followed by concentrated sulphuric acid a green colouration is obtained which finally changes to blue. It dissolves in concentrated sulphuric acid with a yellow colour which finally changes to deep red on warming. With concentrated hydrochloric acid it gives no colouration, but with concentrated nitric acid a bright red colouration is developed on heating. It gives no precipitate with lead acetate or silver nitrate, but with alcoholic ferric chloride a light red colouration is produced. With Tollen's reagent a light yellow coloured solution is formed which slowly changes to brown

and finally a gradual reduction takes place. With alkaline solution of potassium nitroprusside it gives a reddish brown colouration. [Found: C, 74·0, 74·3; H, 3·5, 3·7; M.W. (cryoscopic in phenol) 260, 281. $C_{18}H_{10}O_4$ requires C, 74·5; H 3·4 per cent. M.W. 290].

Isolation of cuscutin.—The combined alcoholic extract after the removal of cuscutalin was concentrated when a thick syrupy greenish red liquid was obtained, smelling of sugars. This was then extracted successively with benzene, ethyl acetate and water.

The benzene extract was deep green in colour and contained a large amount of chlorophyll. This was evaporated to dryness and the dried mass washed repeatedly with cold alcohol and crystallised from boiling alcohol when white flakes of cuscutalin (m.p. 67-68°) were obtained.

The ethyl acetate extract was golden red in appearance and on concentration became very syrupy. Nothing chemically definite could be isolated from it.

After treatment with benzene and ethyl acetate, the original mass was dissolved in ice-cold water with constant stirring. A brown stuff separated (m.p. 140°) which was filtered and washed. It was dissolved in a large quantity of water at the ordinary temperature and the golden yellow solution kept in an ice-chest overnight, when pale yellow crystals separated which were filtered, washed and dried, m.p. 208-9° (decomp.) with previous softening at 179°.

The aqueous extract after the removal of cuscutin as described above, was concentrated and was found to reduce Fehling's solution readily. It contained a large amount of reducing sugars.

Properties of cuscutin.—It is easily soluble in ethyl and methyl alcohols, pyridine and acetic acid, less so in acetone and water and insoluble in benzene, ethyl acetate, chloroform, ether and petroleum ether. The solution in all these solvents has an orange yellow colour. It decomposes if boiled with water. Cuscutin dissolves readily in solutions of alkali carbonates, bicarbonates and hydroxides giving a bright orange-yellow solution, which undergoes dicomposition if boiled. It can, however, be precipitated from these solvents by the addition of dilute mineral acids. With concentrated sulphuric acid a reddish brown colouration is produced with a slight flourescence; with concentrated nitric acid a blood-red colouration is developed which changes to light orange on warming. In concentrated hydrochloric acid it dissolves with an orange-yellow colouration. It produces a geen precipitate with ferric chloride, and yellowish white

precipitate with lead acetate and a white precipitate with silver nitrate. The dilute alkaline solution decolourises a solution of potassium permanganate. It gave a negative test for flavones and was completely decolourised on being boiled with ammonia and zinc dust. It was not glucosidic in character. [Found: C, 53·4, 53·2; H, 3·9, 3·7; M.W. (crysyocopic in phenol) 330, 342, (lead salt) 388. $C_{15}H_{12}O_9$ requires C, 53·6; H, 3·6 per cent. M.W. 336).

Lead salt.—To 0·5 g. of cuscutin dissolved in alcohol, an alcoholic solution of lead acetate was added drop by drop till the yellow precipitate was no longer obtained. The lead salt was filtered, washed thoroughly and dried. It was an yellowish brown stuff. (Found: Pb, 48·07. $C_{30}H_{18}O_{18}Pb_3$ requires Pb, 48·2 per cent).

Diacetylcuscutin was prepared from 1 g. of cuscutin, 25 c.c. of acetic anhydride and a little fused sodium acetate by refluxing for 2 hours. It crystallised from glacial acetic acid as yellowish brown microcrystalline needles, m.p. 140°. [Found: C, 54·1; H, 3·9. $C_{15}H_{10}O_9(C_2H_3O)_2$ requires C, 54·4; H, 3·8 per cent].

Dicarbethoxycuscutin.—1 G. of cuscutin was dissolved in pyridine and an excess of ethyl chloroformate was slowly added with vigorous shaking till the solution had a slight pink colour. It was then poured into water, a black oil separated which solidified on keeping in water to a hard vitreous mass. It was filtered and crystallised from ethyl alcohol as brown crystalline flakes, m p. 151° (decomp.). It dissolved in most organic solvents and gave no colouration with alkalis. [Found: C. 52·9; H, 3·9. $C_{15}H_{10}O_9$ ($C_6H_{10}O_4$) requires C, 52·5; H, 4·2 per cent].

Dimethoxycuscutin.—0·8 G. of cuscutin was dissolved in strong caustic potash and dimethyl sulphate added slowly with constant shaking. More alkali was then added and the mixture cooled in water and shaken vigorously for an hour, when an oily liquid separated which gradually solidified on keeping in cold water. It was filtered and crystallised from alcohol as pale yellow crystalline flakes, m.p. 193°. [Found: C, 55·8; H, 4·9. $C_{15}H_{10}O_7(OMe)_2$ requires C, 56·0; H, 4·4 per cent).

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Metallic Uranium in Organic Synthesis. Part I.

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In continuation of the work on the synthetic use of metals published from these laboratories (Ray and Dutt, *J. Indian Chem. Soc.*, 1928, **5**, 103; Chakrabarti and Dutt, *ibid.*, 1928, **5**, 517; Lal and Dutt, *ibid.*, 1932, **9**, 565) we have now studied uranium from this point of view for the first time, since this metal is now commercially available. The investigation also has a special interest in view of the fact that like the metal thorium which was very successfully used by Gaind and Dutt (*Allahabad University Studies*, 1934, **10**, 297) in organic synthesis, uranium is also a radioactive element, and and as such, is expected to possess high reactivity towards organic reagents.

Uranium has not given very encouraging results in Ullmann's reaction but has proved highly satisfactory in Friedel-Craft's, Reformatsky's and Zincke's reactions. The action of benzyl chloride on benzene, anisol and phenetol in presence of uranium has been successfully tried and the products isolated in good yields. Attempts have been made to study the higher products formed in these reactions, for instance in the case of benzene and benzyl chloride, besides pure diphenymethane isolated in 40% yield, *sym*triphenylethane, *o*- and *p*-dibenzylbenzenes and a trace of a sulphur-yellow hydrocarbon, m. p. 71°, have also been isolated.

Uranium, however, is distinctly more basic than any other member of the 6th group of the Periodic Table. Metallic chromium (*loc. cit.*), molybdenum and tungsten (work in course of publication) have all been tried in organic syntheses in our laboratory. The successful results with chromium have all been obtained with organic chlorine compounds in which the chlorine atoms are rather loosely attached to the molecule and are very reactive. All the three metals cannot be used in either Reformatsky's or Grignard's reaction evidently on account of their much less basic character. In Ullmann's reaction, requiring increased electropositive nature on the part of the metal used for the removal of the halogen atoms, chromium, molybdenum and tungsten all fail, while uranium is very feebly reactive.

Details of the successful experiments are given in the experimental part, while those of the unsuccessful attempts are omitted.

Unsuccessful attempts.

Types of reaction.	Reactants.	Expected product.
Ullmann's	Carbon tetrachloride	Hexachlorethane
Friedel-Craft's	Chloroform and benzene	Triphenymethane
	Carbon tetrachloride and benzene	Triphenyl chloromethane
	Iodobenzene and aniline	Diphenylamine
Grignard's	Uranium and bromobenzene	Uranium phenyl-bromide

EXPERIMENTAL.

Friedel and Craft's Reaction with Uranium Powder.

Diphenyl from benzene and bromobenzene.—Benzene (12 g.), bromobenzene (8·59 g.) and uranium dust (4 g.) were refluxed for 18 hours when a very feeble reaction took place. The yield of diphenyl isolated on fractionation was only 0·19 g., m.p. 68°.

Diphenyl from chlorobenzene and benzene.—The reaction was carried on as above. The yield of diphenyl from uranium (4 g.), chlorobenzene (12 g.) and benzene (18 g.) was only 2 g.

Diphenyl from iodobenzene and benzene.—The reaction was carried on as above. The yield of diphenyl from iodobenzene (12 g.), benzene (18 g.) and uranium (4 g.) was only 0·25 g.

Triphenylmethane from benzalchloride and benzene.—Benzene (30 g.), benzalchloride (12 g.) and uranium dust (4 g.) were refluxed together on a water-bath for 8 hours. The dark violet product was filtered from the metal and fractionated to remove benzene and unchanged benzalchloride. The solid residue left in the flask crystallised from alcohol in needles, m.p. 92°, and was identified as triphenylmethane, yield 0·9 g.

Triphenychloromethane and dichlorodiphenylmethane from benzotrichloride and benzene.—Benzotrichloride ·15 g.), benzene (50 g.) and uranium dust (3 g.) were heated in an oil-bath at 115°-128° when after half an hour's heating a fairly vigorous reaction took place. After heating for 8 hours to complete the reaction, the deep pink mixture was filtered, benzene removed by heating on the water-bath and then fractionated at 35 mm. and the fraction boiling at 198°-203° and redistilled at 200°-202° was identified as dichlorodiphenylmethane (yield 4·2 g.) and the residue in the flask was crystallised from carbon disulphide and melted at 110°-115° and was identified as triphenylchloromethane, yield 1·2 g.

Acetophenone from acetyl chloride and benzene.—Benzene (18 g.), acetyl chloride (12 g.) and uranium dust (3 g.) were refluxed on a water-bath for 6 hours when a moderately vigorous reaction took place. The product was treated with ice-cold hydrochloric acid and the resulting yellow oil extracted with benzene, washed repeatedly with water, dried with anhydrous calcium chloride and fractionated; the fraction at 185-210° (redistilled at 198°-200°) was collected and identified as acetophenone, yield 1·2 g (6·8%).

Benzophenone from benzoyl chloride and benzene.—A mixture of benzoyl chloride (11 g.), benzene (15 g.) and uranium dust (3·5 g.) was heated on the sand-bath under reflux, till the evolution of hydrogen chloride had ceased (8 hours). The mixture was then treated with ice-cold dilute hydrochloric acid and the benzene layer separated. It was washed with strong caustic soda solution repeatedly, and then with water, dried and fractionated at ordinary pressure. The pale yellow oil, distilling at 295°-310°, solidified on keeping for some hours and after crystallisation from alcohol melted at 46° and was identified as benzophenone, yield 2·3 g.

Ullmann's Reaction with Uranium Powder.

Diphenyl from bromobenzene.—Bromobenzene (10 g.) and uranium (8 g.) were refluxed at 170°-180° for 20 hours. The product was filtered and fractionated when after removal of bromobenzene at 155°-164° a very small amount of liquid distilled above 245° and solidified in the receiver. After crystallisation from a little alcohol it melted at 67° and was identified as diphenyl, yield 0·3 g.

Diphenyl from chlorobenzene.—Chlorobenzene (10 g.) and uranium (7 g.) were refluxed at 150°-160° for 20 hours and the product isolated as in the preceding case, yield 0·2 g.

Diphenyl from iodobenzene.—Iodobenzene (10 g.) and uranium (6 g.) were refluxed at 170°-190° for 20 hours and the product isolated as in the preceding cases, yield 0·4 g.

Diethylsuccinate from ethyl bromoacetate.—A mixture of ethyl bromoacetate (10 g.), ethyl acetate (10 g.) and uranium powder (3 g.) was refluxed at 110-120° tor 15 hours and the product filtered, washed, dried and fractionated. The fraction at 200°-220° (redistilled at 216°-218°) was identified as diethylsuccinate, yield 1·4 g.

Adipic acid from β-iodopropionic acid.—When β-iodopropionic acid (10 g.) was heated with uranium (7 g.) first at 100° for 2

hours and then at 160°-165° for 8 hours, a little iodine was liberated. The product was extracted with hot water, filtered, and the filtrate on concentration gave *adipic acid*, m. p. 148°, yield 1·2 g.

Diphenyl ether from phenol and bromobenzene.—A mixture of pure anhydrous phenol (10 g.), bromobenzene (17 g.), uranium dust (3 g.) and freshly heated anhydrous potassium carbonate (0·8 g.) was refluxed at 180°-200° for 12 hours. The filtered product was distilled in steam and the distillate was extracted with ether. The ether extract was washed with dilute caustic soda and then with water, dried over calcium chloride and fractionated. The fraction at 240°-260° (redistilled at 253°-254°) was identified as diphenyl ether, yield 2·9 g.

Succinic acid from sodium chloroacetate and anhydrous sodium acetate.—A mixture of sodium chloroacetate (12 g.), anhydrous sodium acetate (8 g.) and uranium (3 g.) when heated at 110°-120° for 3 hours gave very vigorous reaction. The product was extracted with water and ammonia added in slight excess to precipitate uranium hydroxide. The boiled and neutral filtrate was treated in the cold with neutral ferric chloride when ferric succinate was precipitated. This was filtered, washed with water thoroughly and decomposed by hydrogen sulphide. The filtrate from iron sulphide was evaporated to dryness on a water-bath and extracted with ether. The ethereal extract on complete evaporation gave 1·5 g. of *succinic* acid, m. p. 185°.

Zincke's Reaction with Uranium Powder.

Diphenylmethane and its higher homologues from benzyl chloride and benzene.—A mixture of benzyl chloride (30 g.), benzene (80 g.) dried over sodium, and uranium dust (4 g.) was slowly heated in an oil-bath up to 80° when a very vigorous reaction took place and torrents of hydrogen chloride were evoloved. After the first vigorous reaction had subsided, the mixture was heated at 100-10° for 4 hours. The pink mixture was filtered from the metal and washed first with caustic soda and then with water. After dehydrating over anhydrous calcuim chloride excess of benzene was removed on the water-bath and then fractionated. The fraction at 250°-280° was redistilled thrice and finally the portion distilling at 258°-261° was identified as diphenylmethane. It was a non-flourescent colourless liquid having an orange like smell and solidified on keeping in ice in thin radiating needles, m.p. 26°, [m.p. of pure diphenylmethane is 26·5° in literature and 28° by Smithe (*J. Chem. Soc.*, 1922, **121**, 1276) and gave on

oxidation with alkaline potassium permanganate benzophenone, m. p. 47°. (Found: C, 92·34; H, 7·39. Calc. for $C_{13}H_{12}$: C, 92·85; H, 7·14 per cent).

The thick residual oil in the distilling flask was then fractionated under reduced pressure (14 mm.) and the first fraction (210°-260°) and the second (260-360)° were collected and then there was left a highly coloured and exceedingly viscous liquid which set to a hard, gum-like mass on cooling but softened and fused again on gentle warming. The first fraction had a violet fluorescence and on keeping overnight became semisolid which after removal of the oily portion by spreading on porous plate melted at 50-70°. By repeated crystallisation from alcohol, acetone and benzene in succession it was separated into two constituents; one, consisting of the more soluble fraction, m. p. 81-84° and the other m. p. 53-54°, b.p. 396°-400° at ordinary pressure identified to be *sym*triphenylethane. (Found: C, 92·75; H, 7·12. Calc. for $C_{20}H_{18}$: C, 93·02; H, 6·98 per cent.) and that melting at 81°-84° was found to be a mixture of *o*- and *p*-dibenzylbenzenes and as the quantity of the mixture was only 4·9 g. the complete separation of the two isomers was not possible. A small amount of sulphur-yellow hydrocarbon which on recrystallisation from alcohol melted 71° was also obtained (*cf. J. Chem. Soc.*, 1922, **121**, 1278). Yield of dipenylmethane was 18·4 g. (40%), of *sym*triphenylethane was 3 g., of dibenzylbenzene was 4·9 g. and that of yellow hydrocarbon was 1 g. and about 5 g. of deep brown viscous residue were left in the distilling flask.

Phenetolyl-phenylmethane from phenetol and benzyl chloride.—A mixture of phenetol (20·4 g.), benzyl chloride (18·0 g.) and uranium dust (3·5 g.) was gradually heated in an oil-bath. A very vigorous reaction commenced at 70° and was completed by heating for 2 hours at 130° after the first vigourous reaction had subsided. The pink product having an intense violet fluorescence was extracted with benzene, filtered and the filtrate washed with caustic soda and water. The alkaline washings gave nothing on acidification and extraction with ether, showing that no demethylation had taken place during the course of the reaction as in the reactions with alkyl ethers of phenolic compounds in presence of anhydrous $AlCl_3$. The well washed benzene layer was dried over calcium chloride and fractionally distilled, the fractions above 300° being collected: (*i*) 305°-315°, (*ii*) 315°-345°, (*iii*) 345°-370°. The temperature then rose very quickly and (*iv*) a deep red liquid was left in the distilling flask (5 g). The fraction (*i*) and (*ii*) were combined and redistilled, the fraction distilling at 330°-345°

(redistilled at 338°-341°) was identified as *p*-ethoxydiphenylmethane, yield 24·2 g. (80%). (Found: C, 84·64; H, 7·64. Calc. for $C_{15}H_{16}O$: C, 84·92; H, 7·55 per cent). The residue left in the flask was an exceedingly thick liquid and nothing definite and crystalline could be obtained from it.

Anisoylphenylmethane from anisole and benzyl chloride.—A mixture of anisole (22 g.), benzyl chloride (21 g.), and uranium dust (3 g.) was gradually heated in an oil-bath up to 70° when a very vigorous reaction took place and after it had subsided the mixture was heated at 120°-130° for 3 hours. The pink reaction product having an intense violet fluorescence was extracted with hot benzene, filtered and the filtrate treated first with 5% caustic soda and then with water. The alkaline washing gave nothing after acidification and extraction with ether. The well washed benzene layer was separated, dried over calcium chloride and fractionated, the fractions distilling above 290° were collected: (*i*) 290°-315°, (*ii*) 315°-370°, and (*iii*) 370°-380°.

Fraction (*i*) (redistilled at 303°-305°) was identified to be anisoylphenylmethane (yield 17·4 g 52·9%.) (*cf.* Rennie, *J. Chem. Soc.*, 1882, **41**, 227). (Found: C, 84·41; H, 7·12. Calc. for $C_{14}H_{14}O$: C, 84·84; H, 7·07 per cent) and the fraction distilling at 370°-380° was redistilled when most of it distilled at 376°-382° and was a very thick liquid with a very intense greenish blue fluorescence. (Found: C, 86·2; H, 7·12. $C_{21}H_{20}O$ requires C, 87·5; H, 6·94 per cent). It is probably dibenzylanisole (yield 6·9 g.).

Reformatsky's Reaction with Uranium Powder.

A mixture of acetophenone (12 g.), dried over metallic sodium, bromoacetic ester (17 g.), uranium dust (35 g.) and dry benzene (70 c. c.), dried over sodium, was gently warmed on the water-bath when a feeble reaction took place. After addition of a crystal of iodine the mixture was refluxed in an oil-bath at 120°-130° for 10 hours, by which time the mixture had become a pasty mass. After cooling, ice-cold dilute hydrochloric acid was added to decompose the complex compound, the benzene layer separated, washed with dilute caustic soda and with water, dried over calcium chloride, and then fractionally distilled under highly reduced pressure. The fraction at 112°-130°/13 mm (redistilled at 118°-121°) was identified as phenylmethyl hydroxypropionic ester, yield 2·4 g.

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Vasicine *

By Mohan Lal Beri, Kartar Singh Narang and Jnanendra Nath Rây.

Späth and Nikawitz (*Ber.*, 1934, **67**, 45) isolated an alkaloid $C_{11}H_{12}ON_2$ from *peganum harmala* which resembled vasicine in its melting point and other properties but the solubility of the alkaloid in acetone was not similar to that of vasicine. Vasicine crystallises from hot acetone whilst peganine was found to be more soluble. Hanford, Liang and Adams (*J. Amer. Chem. Soc.*, 1934, **56**, 2780) have determined the solubility of the alkaloid in acetone and found it to be small. The greater solubility of peganine in acetone may be due to associated impurities. Narang and Rây (*Current Science*, 1934, **2**, 388) stated that vasicine is not precipitated from the solution of its hydrochloride by alkali till acidified with acetic acid. Hanford *et al* (*loc. cit.*) have found that vasicine is no more soluble in alkali than in the corresponding volume of water. The solubility of vasicine in the alkaline solution noticed by Narang and Rây was due to its retention in solution as a colloid.

There is no doubt as to the identity of vasicine and peganine, hence the name peganine is redundant (Reynolds and Robinson, *Nature*, 1934, **134**, 142).

It has never been seriously suggested by us that vasicine and peganine are different. The question of identity of the two was left open by Späth. We had no peganine at our disposal but from its properties, *e.g.*, the solubility in acetone, etc., described by Späth we thought that the two may be different. The question of the acetyl derivative is a puzzling one. We have obtained a solid acetyl derivative from vasicine but its formation may be due to a profound change in the molecule, *e.g.*, the acetyl may be formed by the tautomerism of a hydrogen atom to the nitrogen atom of the amidine system as is the case in harmaline and a loss of a molecule of water from the alcoholic hydroxyl and a hydrogen atom from a neighbouring carbon atom.

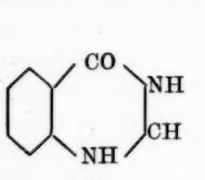
* The paper was received for publication on April 29, 1935 and Prof. Späth's paper dealing with the same subject (*Ber.*, 1935, **68**, 699) was not available in India till 7th May.—Editor.

The structure (I) for vasicine was advanced by Ghosh, Krishna, Narang and Rây (*J. Chem. Soc.*, 1932, 2740) mainly on the ground of its giving 4-oxyquinazoline by oxidation and anthranilic acid by potash fusion. The presence of an *allyl* group was suspected because of its ready reduction of a dilute permanganate solution. Späth and Nikawitz (*loc. cit.*) relied on the same test and postulated an allyl grouping in the formula (II) they advanced. It is quite unsafe to postulate an allyl grouping as it has now been proved that a secondary alcohol grouping exists in vasicine and the reduction of permanganate is due to this. Recent experiments have indicated (*cf.* Narang and Rây, *Current Science*, 1935, **3**, 352) that vasicine has a cyclic structure. Full experimental details are in course of preparation.

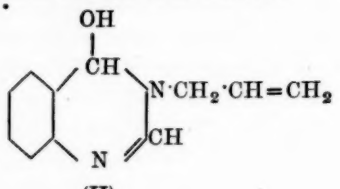
However, the results of Narang and Rây (*Current Science*, *loc. cit.*), Reynolds and Robinson (*loc. cit.*), Hanford *et al* (*loc. cit.*) conclusively dispose of the formula (II) proposed by Späth *et al.*

The present experiments on the synthesis of vasicine were initiated when the structure (I) was thought to be probable. Späth and Nikawitz (*loc. cit.*) found that peganine on reduction with sodium and amyl alcohol gave a low melting base. 4-Oxyquinazoline (III) gave with allyl iodide the substance (IV) which on reduction with sodium and amyl alcohol gave an oily base not identical with the base obtained by Späth *et al* (*cf.* Narang and Rây, *Current Science*, *loc. cit.*, Hanford *et al*, *loc. cit.*).

α-Bromobutyranilide (V) did not condense with urethane to give a quinazoline and was converted into crotonanilide in poor yield by hot dimethylaniline. But action of alcoholic potash converted it into the interesting substance β-ethylindolenone (VI).



(I)



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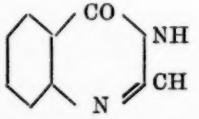

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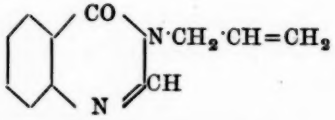
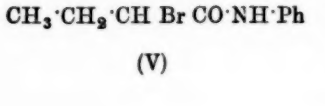
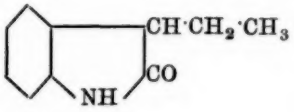


(IV)

Treatment of (V) with moist silver oxide led to α-hydroxybutyranilide but this also did not condense with urethane. Itaconic anhydride condensed with aniline to give (VII).



(V)



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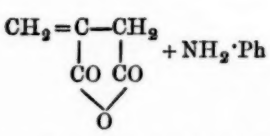
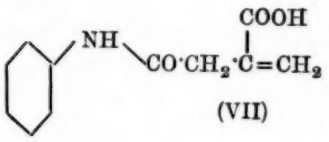
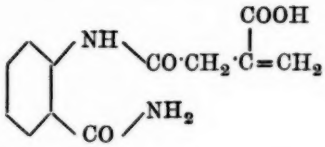




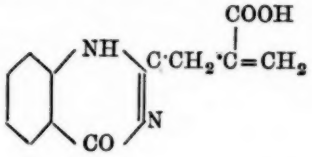
(VII)

It was thought that this substance after condensation with urethane and decarboxylation would furnish (I) but the initial reaction with urethane here also was unsuccessful.

o-Aminobenzamide, however, gave the substance (VIII) on interaction with itaconic anhydride which easily cyclised to (IX), but its



(VIII)



(IX)

decarboxylation did not proceed satisfactorily.

Experimental.

4-Oxyquinazoline (5·4 g.), allyl iodide (1·5 mols.) and alcoholic potassium hydroxide (10%, 1·2 mols.) in alcohol (54 c.c.) was refluxed on the steam-bath for 3 hours. The volume was concentrated to 15 c.c. and made strongly alkaline when an oily substance separated. It was extracted with ether (2 0 c.c); the residue from ether solidified. It crystallised from hot petroleum ether in clusters of needles, m.p. 67°. (Found: N, 14·96. $C_{11}H_{10}ON_2$ requires N, 15·05 per cent).

0·5 G. of the above substance was distilled in steam for 30 minutes and the distillate extracted repeatedly with ether. The ethereal

solution furnished nothing indicating that the allyl group is attached to the nitrogen atom and not to the oxygen atom (*cf. J. Amer. Chem. Soc.*, 1909, **31**, 506).

Treatment of the above substance with hydrochloric acid.—0·5 G. of the above 3-allyl-4-oxyquinazoline was dissolved in hydrochloric acid (*d* 1·16, 10 c.c.) and was heated at 110° for 2 hours when 5 c.c. more of the acid were introduced. The product was made alkaline and extracted with ether. The extract on concentration yielded 0·45 g. of the original substance (m.p. and mixed m.p.). This also proves that it is not an *O*-allyl ether.

Reduction of 3-allyl-4-oxyquinazoline with sodium and amyl alcohol.—The substance (2 g.) dissolved in amyl alcohol (100 c.c.) was reduced with sodium (8 g.) slowly under reflux. The final colour of the solution was pale yellow. It was decomposed with water (100 c.c. contact for 12 hours).

After acidification, the amyl alcohol was removed by steam distillation and the residue after extraction with ether was cooled to 0° and basified. The separated material was extracted with ether whence a liquid, b. p. 105°-108°/3 mm., was isolated. For analysis and other details *cf.* Hanford *et al* who have repeated this experiment since our publication in *Current Science*.

Treatment of α-bromobutyranilide with alcoholic potash.—The anilide (3·6 g.) dissolved in alcohol (50 c.c.) was treated with a solution of potassium hydroxide (1·2 mols.) in the smallest amount of water at 50°. A colourless substance (1·5 g.) separated after 20 minutes and was collected after 3 hours. After treatment with water it was crystallised from benzene in delicate colourless needles, m.p. 264°-65°. (Found: C, 74·25; H, 6·98; N, 8·75. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8; N, 8·7 per cent).

The bromoanilide (14 g.) dissolved in acetone (50 c.c.) was refluxed with silver oxide (from 17 g. of silver nitrate) for 9 hours. The filtrate on concentration furnished an oil which solidified on standing. Crystallised from water it separated in colourless needles, m.p. 89°-90°. (*cf. Annalen*, 1894, **279**, 104). The condensation of α-hydroxybutyranilide with urethane did not succeed.

Condensation of o-aminobenzamide with α-bromobutyryl bromide.—*o*-Aminobenzamide (1 g.) dissolved in benzene (20 c.c.) was treated with pyridine (0·7 g.) and a solution of α-bromobutyryl bromide (1·85 g.) in benzene (10 c.c.). The mixture was treated with water after the abatement of the vigorous reaction and the product

was crystallised from hot benzene in fine needles, m.p. 144°. (Found: N, 9·56. $C_{11}H_{13}O_2N_2Br$ requires N, 9·82 per cent).

The above product (0·47 g.) was treated with sodium hydroxide (0·2 g. in 1 c.c. of water and 15 c.c. of alcohol) and heated to 50° for 10 minutes and then diluted with water and acidified with acetic acid. The product (2-α-bromopropyl-4-oxyquinazoline, 0·3 g.), crystallised from alcohol in fine colourless needles, m.p. 218° (decomp.). (Found: N, 10·20. $C_{11}H_{11}ON_2Br$ requires N, 10·48 per cent).

The above 2-bromopropyl-4-oxyquinazoline (0·5 g.) was reduced with zinc dust (5 g.) in 20 c.c. of 3% sodium hydroxide solution. The alkaline filtrate on acidification with acetic acid furnished 0·2 g. of 2-propyl-4-oxyquinazoline, m.p. 200° (mixed m.p. with an authentic specimen) after crystallisation from hot dilute alcohol.

o-*Nitrobenzamide*.—o-Nitrobenzoyl chloride (6 g.) was slowly powdered with ammonium carbonate (16 g.) and warmed on the steam-bath for 2 hours. The product treated with much water furnished the *amide* (5 g.). After crystallisation from hot water, the yield is much better than recorded in literature, m.p. 176°.

o-*Aminobenzamide*.—To a solution of stannous chloride (6 g.) in hydrochloric acid (*d* 1·16, 6 c.c.) finely powdered o-nitrobenzamide (2 g.) was added in small portions with stirring, the temperature being kept at 50°-65° during the reduction for an hour. The separated double compound was collected, dissolved in water and strongly basified. After extraction with ether the solvent was distilled off, yield 1·2 g., m.p. 110°.

Condensation of o-aminobenzamide with itaconic anhydride.—The *amide* (1 g.) dissolved in dry benzene (50 c.c.) was mixed with itaconic anhydride and refluxed for an hour. The colourless substance separating was collected and crystallised from water, m.p. 174°-76° (decomp.). [Found (after drying in high *vacuo* at 100°): C, 58·0; H, 4·9; N, 11·23. $C_{12}H_{12}O_4N_2$ requires C, 58·07; H, 4·84; N, 11·29 per cent].

The above product (1·2 g.), dissolved in sodium hydroxide solution (5%, 20 c.c.), was warmed to 50° for 45 minutes. It was then cooled and acidified with acetic acid when a colourless substance separated. After crystallisation from dilute alcohol in delicate silky needles, it had m.p. 197°-98°. [Found (in material dried in high *vacuo* at 100°): C, 63·0; H, 4·48; N, 11·84. $C_{12}H_{10}O_3N_2$ requires C, 63·29, H, 4·35; N, 12·17 per cent].

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On the Supposed Occurrence of Acids with Uneven Number of Carbon Atoms in Vegetable Oils and Fats. Part I. Daturic Acid from the Seeds of *Datura Stramonium*, Linn.

By B. L. Manjunath and S. Siddappa.

The vast majority of fatty acids isolated from vegetable oils and fats are found to contain an even number of carbon atoms. However, in the literature, many instances have been reported of the occurrence of fatty acids with an odd number of carbon atoms. The existence of such acids has always been looked upon with considerable doubt and the occurrence of none of them has been questioned by later investigators.

The acid $C_{17}H_{34}O_2$, known as daturic and margaric acids, has been said to occur very widely in oils and fats. The earliest mention of this acid is by Gerand (*Compt. rend.*, 1880, **111**, 305). He claims to have obtained it by the fractional precipitation of the solid acids from the oil of *Datura stramonium* seeds. Holde (*Chem. Zentr.*, 1902, **II**, 1417) confirmed the presence of this acid in the above source, but questioned its individuality a little later (Holde, Ubbelonds, and Marcusson, *Ber.*, 1905, **38**, 1347). Meyer and Beer (*Monatsh.*, 1918, **33**, 311), as a result of detailed investigations, claim to have definitely established the individuality of daturic acid, as well as its identity with margaric acid. In view of this work Elsdon ("Edible oils and fats", 1926, p. 30) has stated "This is the only acid with an uneven number of carbon atoms, that has been definitely proved to exist in an oil. It is one which is, therefore, of great theoretical interest and which may very well repay further study."

Reference must be made next to the work of Verkade and Coops (*Biochem. Z.*, 1929, **206**, 468) on the methyl esters of the solid acids from the oil of *Datura stramonium*. They subjected these to fractional distillation in vacuum and from a comparative study of the

melting points of the various fractions with those of the synthetical mixtures of the methyl esters of palmitic and stearic acids, they concluded that daturic acid is really a mixture of palmitic and stearic acids.

The chief difficulty in investigations of this nature arises from the fact that fatty acids are apt to form eutectic compounds, behaving as regards melting and solidifying points, like pure chemical substances, which cannot be easily resolved into their components either by fractional precipitation or crystallisation (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Ed. Vol. I, pp. 118-21 ; Francis, Piper and Malkin, *Proc. Roy. Soc.*, 1930, **A123**, 214). The ternary system, palmitic, synthetical margaric and stearic acids has recently been studied by Schriner, Fulton and Burks. (*J. Amer. Chem, Soc.*, 1933, **55**, 1494). The curve for palmitic and stearic acids indicates the formation of a compound, very close to the equimolecular ratio at 57·5°. The freezing points of margaric acid with the equimolecular mixture have also been studied. The drop in the freezing point is not very great. Although this drop could be easily detected by accurate melting point determinations, it will pass unnoticed in the ordinary mixed melting point determinations. Since the melting points given in the literature for daturic acid vary from 54° to 60°, it can be easily seen how an approximately equimolecular mixture of palmitic and stearic acids may be mistaken for daturic acid and also why mixed melting points are not conclusive evidence for identification.

By intensive fractionation of the methyl esters, Francis, Piper and Malkin (*loc. cit.*) have been able to separate mixtures of solid acids into nearly chemically pure acids and when this method was applied to the separation of the solid acids of the oil of *Datura stramonium*, they were found to consist of palmitic and stearic acids together with small quantity of lignoceric acid. No trace of daturic acid could be obtained.

Experimental.

For purposes of this investigation, the seeds were specially grown and collected under careful supervision. The oil content was found to be 16·3%. About 6·2 kg. of the seeds were extracted with petroleum ether (b.p. 50°-60°) in a large soxhlet. On distilling off the solvent 1020 g. of a pale yellow oil were obtained.

TABLE I.

Physical and chemical constants of the oil.

Sp. gr. at 25°	0·9181	Acetyl value	25·6
n at 25°	1·4735	Reichert-Miesel value	0·44
Saponification value	187·1	Total fatty acids	87·7
Iodine value (Hanus)	122·6	Percentage of unsaponifiable matter	2·6
Acid value	5·6		

The oil (1 kg.) was saponified with sodium hydroxide. The resulting soap, after extraction with ether to obtain the unsaponifiable matter, was dissolved in water and acidified with hydrochloric acid when the insoluble fatty acids (855 g.) were liberated. These were separated into the saturated and unsaturated acids by Twitchell's method (*Ind. Eng. Chem.*, 1931, **13**, 806).

TABLE II.

Chemical constants of the fatty acids.

Mean M. W. of mixed acids	289·1	Mean M. W. of solid acids	263·2
Iodine value of mixed acids	120·7	Mean M. W. of liquid acids	304·4
% of solid acids	13·1	Iodine value of liquid acids	126·5

The unsaturated acids.—The unsaturated acids were obtained as a yellowish brown oil. They were purified by the distillation of their methyl esters under diminished pressure.

10 G. of the acids were oxidised with cold dilute permanganate (Lewkowitsch, *loc. cit.*, Vol, I, p. 575). The mixture of insoluble hydroxy acids was filtered and dried. From the filtrate no hexahydroxy acid could be isolated. On extracting the dried precipitate with ether in a small soxhlet, dihydroxystearic acid (m.p. 136°, M. W. 316·1) was obtained. The residue left after extraction of the dihydroxy acid was treated with 5—6 litres of boiling water and the aqueous extract on cooling deposited crystals of tetrahydroxystearic acid (m.p. 172°-73°, M. W. 352).

Another 10 g. of the acids were treated with bromine according to the method of Eibner and Mugenthaler (Lewkowitsch, *loc. cit.*, Vol. I., p. 585). No other insoluble compound was obtained. From the ether soluble compounds, tetrabromostearic acid (m.p. 113-14°, M.W. 597·1) was obtained.

The above results establish the presence of oleic and linolic acids among the unsaturated acids.

Unsaponifiable portion.—The unsaponifiable matter was dissolved in 95% alcohol and treated with decolourising charcoal. After repeated crystallisations, a phytosterol (m.p. 134°) was obtained. Its acetate melted at 129°.

The saturated acids.—The saturated acids (110 g.) were almost colourless and their methyl esters (111 g.) were subjected to fractional distillation under reduced pressure. Each fraction was then carefully refractionated in high vacuum several times and the following fractions were finally obtained:

TABLE III.

Fraction.	Range of temperature.	Wt. of ester.	Mean M. W. of acids from saponification value.
1	up to 152°	2·75 g.	258·3
2	152°-55°	82·2	256·2
3	155°-57°	0·70	...
4	157°-60°	0·20	...
5	160°-65°	5·50	255·0
6	165°-70°	2·20	263·1
7	170°-72°	10·60	278·6
8	above 172°	1·80	283·9
	Total distillate	105·95	
9	Residue and loss	5·05	

Fractions 1 to 5, weighing 91·35 g. consisted of pure methyl palmitate and on saponification gave palmitic acid (m.p. 61°, M. W. 256).

From fraction 6, a small quantity of pure stearic acid (m.p. 68°, M. W. 284·3) was obtained. The mother liquors gave palmitic acid (m.p. 61°, M. W. 257). Fraction 7 yielded 6 g. of pure stearic acid (m.p. 70°, M.W. 258). The residues from the above were concentrated and some more stearic acid (m.p. 69°; M. W. 282·8) was isolated. Fraction 8 was found to be pure methyl stearate.

The residue 9 was coloured. The liberated acid was dissolved in alcohol and boiled with charcoal. After two crystallisations about 3 g. of an acid melting at 71° (M.W. 356·5) were obtained. The acid on repeated crystallisations melted at 76-77° and had a molecular weight of 371. Its *p*-phenylphenacyl ester was prepared according to the

method of Drake and Bronitsky (*J. Amer. Chem. Soc.*, 1930, **52**, 3715). The ester melted at 101·2° and its melting point was not altered by mixing it with a pure sample of the *p*-phenylphenacyl ester of lignoceric acid.

SUMMARY.

As a result of the detailed chemical examination of the oil from the seeds of *Datura stramonium*, the following constituents were identified:

Unsaturated acids—Oleic and linolic acids.

Saturated acids—Palmitic and stearic acids together with a small quantity of lignoceric acid. No daturic acid could be detected.

A phytosterol, melting at 134°, was obtained from the unsaponifiable matter.

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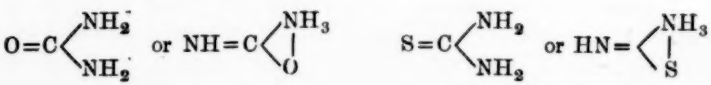
Parachor and Chemical Constitution. Part III. The Structure of Urea and Thiourea.

BY SUSIL KUMAR RAY.

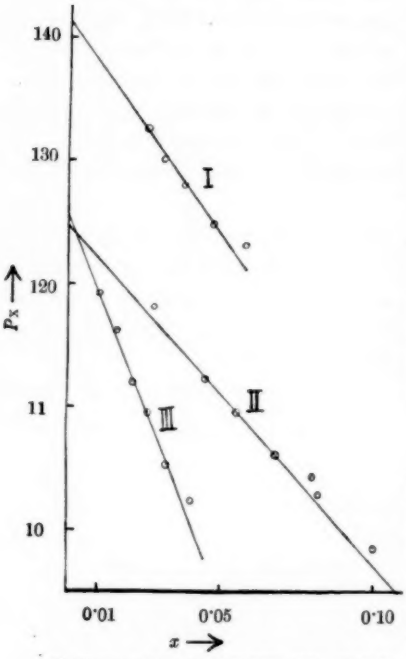
The extensive researches carried out by Werner ("The Chemistry of Urea," Longmans, Green & Co., London, 1923) led him to doubt the validity of the carbamide formula, so universally accepted by chemists to represent the constitution of urea, and to propose a cyclic formula for urea (and thiourea) in the static condition or when present in a neutral solvent.

The object of the present investigations is to find out which of the following two structures agrees with the parachor contribution of the urea and thiourea molecules:



P_{calc}	141·4	158·1	169·6	186·3

The surface tension was determined by the method of maximum bubble pressure as in the previous works. In these experiments, xylene was employed as the manometer liquid, instead of alcohol, and was found to give better results. As the compounds decompose on fusion, the surface tension and density were determined in solution and the parachor calculated from the results obtained (*cf.* Ray, *J. Indian Chem. Soc.*, 1934, **11**, 671).



I—Formamide; II—MeOH; III—EtOH.

The parachor study of urea and of thiourea particularly in solution was found to be extremely limited owing to the lack of suitable solvents. It will be seen that in aqueous solutions constant parachor values were obtained in low concentrations. With increase of concentration after a certain limit, the parachor was found to diminish owing probably to association between the solute and the solvent molecules. In formamide, methyl alcohol and ethyl alcohol, the parachor was found to increase with the increase of x. In these cases the required values are obtained by drawing curves, by plotting P_x against x, and finding its point of intersection with the x axis. In pyridine the values are also not constant. With increasing concentration of the solute, the parachor increases and becomes some what constant.

It will be evident from the results given in the following tables that the parachor contributions of urea and thiourea in aqueous solution and of urea in formamide agree with the carbamide structure. The parachor value of urea, both in methyl and ethyl alcohols, was found to be about 125. This low value is supposed to be due to association between the solute molecules or between the solute and the

solvent molecules. This was corroborated by determining the molecular weight of urea in methyl and ethyl alcohols by Will and Bredig's method of the lowering of the vapour pressure (*Ber.*, 1889, **22**, 1084). It was found that the molecular weight of urea in alcoholic solution is not normal but increases rapidly with increase of concentration. But the exact molecular weight cannot be definitely settled, hence no deduction can be drawn from these results. In pyridine the value was found to be about 144 and here also it is not possible to arrive at any definite conclusion.

In the following tables, x denotes the mol fraction of the solute, M_m, the mean M. W. of the solution, P_m, the mean parachor and P_x, the parachor of the solute. The values within parentheses are obtained from the curves given in the previous page. The observations were carried out between the temperature of 28-30°.

TABLE I

Urea in water.

$P_{calc.}$ for open and ring structure are respectively 141·4 and 158·1.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·9991	74·56	18	52·94	—
0·01326	1·009	74·69	18·56	54·09	139·5
0·01862	1·012	74·71	18·79	54·59	141·3
0·02125	1·014	74·77	18·90	54·81	141·2
0·02344	1·016	74·74	18·99	54·99	140·4
0·03556	1·024	74·85	19·49	55·94	137·3
0·03701	1·028	75·09	19·56	56·01	138·7
0·03806	1·031	75·11	19·60	56·03	134·0
0·05921	1·047	75·34	20·44	57·49	135·7
0·06868	1·054	75·48	20·83	58·41	132·8
0·08443	1·068	74·99	21·55	59·39	129·2

TABLE II.

Urea in formamide.

$P_{calc.}$ for open and ring formulae are respectively 141·4 and 158·1.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	1·159	62·67	45	109·2	—
0·02622	1·662	62·64	45·39	109·8	132·6
0·03101	1·164	62·60	45·46	109·8	129·0
0·03824	1·166	62·58	45·58	110·0	128·1
0·04735	1·168	69·47	45·70	110·0	124·7
0·05853	1·171	62·37	45·87	110·1	123·0
1·0	—	—	—	—	(141·8)

TABLE III.

Urea in methyl alcohol.

$P_{calc.}$ for open and ring formulae are respectively 141·4 and 158·1.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·7883	22·32	32	88·22	—
0·02880	0·8060	22·94	32·81	89·10	118·4
0·04509	0·8244	23·98	33·26	89·30	112·2
0·05480	0 8320	24·21	33·53	89·39	109·5
0·06756	0·8416	24·32	33·89	89·43	106·1
0·08000	0·8503	24·42	34·24	89·50	104·3
0·08194	0·8531	24·55	34·29	89·45	103·4
0·1028	0·8708	24·67	34·88	89·10	98·51
1·0	—	—	—	—	(125·0)

TABLE IV.

Urea in ethyl alcohol.

$P_{calc.}$ for open and ring formulae are respectively 141·4 and 158·1.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·7829	21·86	46	127·1	—
0·01037	0·7882	22·11	46·15	127·0	119·4
0·01547	0·7911	22·25	46·22	126·9	116·3
0·02054	0·7934	22·28	46·29	126·8	112·0
0·02554	0·7950	22·30	46·36	126·7	109·6
0·03232	0·7997	22·30	46·45	126·3	105·2
0·04067	0·8039	22·45	46·57	126·1	102·3
1·0	—	—	—	—	(125·7)

TABLE V.

Thiourea in water.

$P_{calc.}$ for open and ring formulae are respectively 196·6 and 186·3.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·9988	74·41	18	52·94	—
0·002949	1·002	74·30	18·18	53·27	169·2
0·005832	1·004	74·31	18·33	53·62	168·1
0·005883	1·004	74·36	18·34	53·63	169·8
0·007028	1·006	74·43	18·41	53·75	168·0
0·009674	1·009	74·56	18·56	54·06	169·3
0·01085	1·012	74·98	18·63	54·20	169·6
0·01396	1·015	75·03	18·81	54·55	168·4
0·01457	1·016	75·10	18·85	54·62	168·6
0·01738	1·019	75·01	19·01	54·92	166·9
0·01791	1·020	74·99	19·04	54·94	164·7

TABLE VI.

Thiourea in pyridine.

$P_{calc.}$ for open and ring formulae are respectively 169·6 and 186·3.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·0	0·9738	36·11	79	198·8	—
0·02054	0·9835	36·51	78·94	197·2	121·7
0·03247	0·9874	36·75	78·89	196·7	135·5
0·04214	0·9904	36·89	78·88	196·3	140·1
0·06132	0·9979	37·58	78·82	195·5	145·2
0·07741	1·005	37·82	78·77	194·4	142·1
0·08561	1·007	37·87	78·75	194·1	143·6
0·09493	1·012	38·45	78·70	193·7	145·4
0·1019	1·015	38·16	78·69	192·8	140·4

SUMMARY.

The surface tension and density of urea and thiourea were determined in solution and the parachor calculated. The parachor values were found to agree with the carbamide structure.

My grateful thanks are due to Prof. P. R. Rây of the University College of Science and Prof. A. Maitra of the Presidency College for the kind interest they took in the work.

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Studies in Diphenyl Series. Part I. Synthesis of Unsymmetrical Derivatives of Diphenyl.

By Nripendranath Chatterjee.

Hirsch prepared 4- and 2-hydroxydiphenyl by reacting the diazonium salt of benzene with phenol (*Ber*, 1890, **23**, 3705).

The present paper describes an extension and modification of Hirsch's method for the synthesis of diphenyl derivatives. It involves the reaction of an aromatic diazonium salt with a phenol under conditions in which nitrogen is eliminated to yield a diphenyl derivative and a diphenyl ether as a by-product.

The solution of diazonium salt was added to a phenol at 95° and the reaction product was subjected to fractional distillation with superheated steam when the following fractions were obtained:

(*i*) The first fraction consisting of the unreacted phenol.

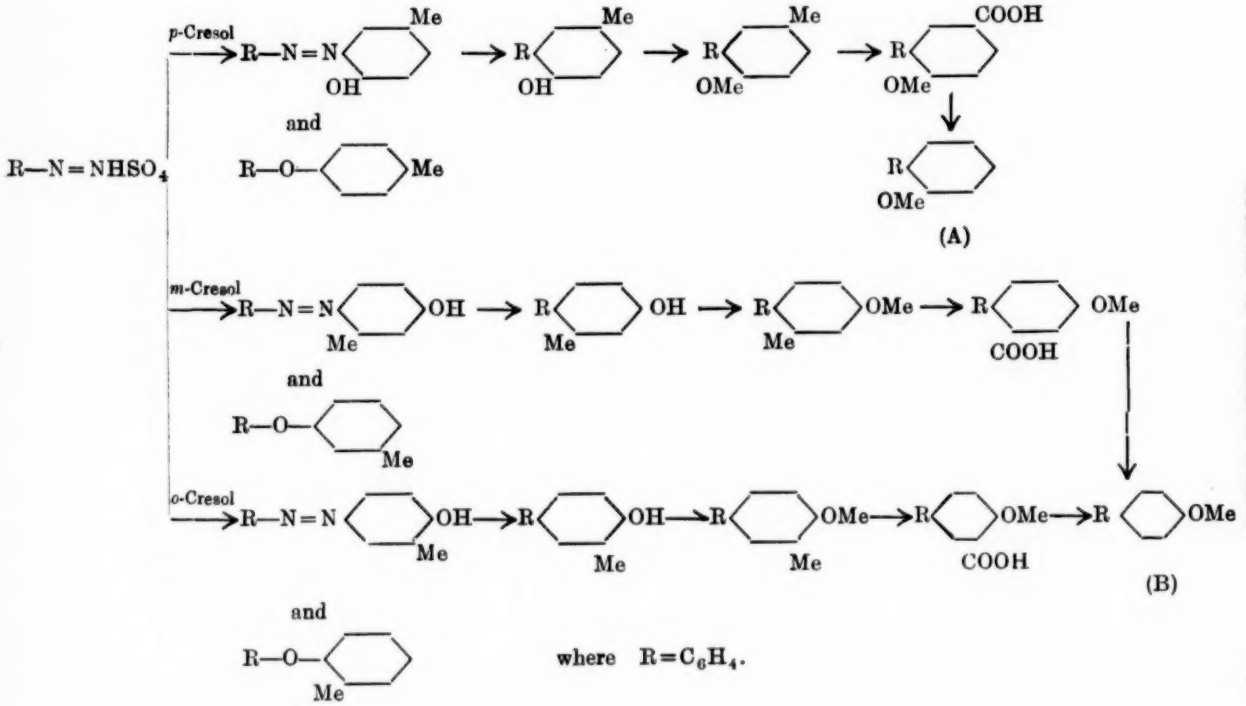
(*ii*) The second fraction consisting of the phenol ether.

(*iii*) The third fraction consisting of a mixture of the phenol ether and the diphenyl derivative.

(*iv*) The fourth fraction consisting of the pure diphenyl derivative.

As regards the constitution of the diphenyl derivatives the position of the methyl group (when toluidines were used) in one of the benzene ring is settled automatically from the nature of the aromatic amine used. The position of the two groups in the other ring will depend on the nature of the linking (either *para* or *ortho*) to the OH group. It was established as follows:

The methyl ether, obtained by means of dimethyl sulphate, was oxidised with neutral permanganate in the usual manner to methyl ethers of the correspondibg acids (monobasic or dibasic) from which the carboxyl group was removed by heating with lime to give the known 2-methoxy- (A) and 4-methoxydiphenyl (B):


p-Cresol
R—N=NHSO4
R—N=N
Me
OH
R
OMe
COOH
and
R—O—
(A)
m-Cresol
o-Cresol
(B)
where R=C6H4.

The compounds obtained from (*o*-,*m*-, *p*-) diazonium salt of toluene with cresols (*o*-,*m*-,*p*-) together with the oxidation products of their methoxy derivatives are given below:

Amine and phenol.	Diphenyls obtained.	Diphenyls obtained on oxidation.
o-Toluidine +		
o-Cresol.	4-Hydroxy-2′ :3-dimethyl-	4-Methoxy-2′ :3-dicarboxy-
m-Cresol.	4-Hydroxy-2′ :2-dimethyl-	4-Methoxy-2′ :2-dicarboxy-
p-Cresol.	2 Hydroxy-2′ :5-dimethyl-	2-Methoxy-2′ :5 dicarboxy-
m-Toluidine +		
o-Cresol.	4-Hydroxy-3′ :3-dimethyl-	4-Methoxy-3′ :3-dicarboxy-
m-Cresol.	4-Hydroxy-3′ :2-dimethyl-	4-Methoxy-3′ :2-dicarboxy-
p-Cresol.	2 Hydroxy-3′ :5-dimethyl	2-Methoxy-3′ :5-dicarboxy-
p-Toluidine +		
o-Cresol.	4-Hydroxy-3′ :4′-dimethyl	4-Methoxy-3′ :4′-dicarboxy-
m-Cresol.	4-Hydroxy-2 :4′-dimethyl-	4-Methoxy-2 :4′-dicarboxy-
p-Cresol.	2-Hydroxy-5 :4′-dimethyl-	2-Methoxy-5 :4′-dicarboxy-

The yields of the diphenyl derivatives are 10-15%. Of the phenyl-ethers prepared 3:4′-dimethyl-, 2:4′-dimethyl,- and 2:3′-dimethyl-phenyl ethers have been prepared for the first time. As the yield of the ethers in all the cases is high, it may be pointed out that this method is also equally suitable for the preparation of the compounds of this type.

Of the hydroxymethyldiphenyls described, only 4-hydroxy-3-methyldiphenyl is previously described in the literature (*Ber.*, 1922, **65**, 1382), which was prepared from 3-methyldiphenyl by sulphonation and subsequent alkali fusion and there is no definite proof about the position of the OH group.

Though these diphenyl derivatives are not able to throw much light on the stereochemistry of the diphenyls, they are useful in another way. As the *pp*′-positions are definitely known to be occupied in some of them, these would on nitration or halogenation, cause the nitro or halogen group to be attached only at the *oo*′-position and as such would be more easily resolvable.

Experimental.

Decomposition of benzenediazonium sulphate with cresol (ortho).—The diazo compound was prepared by treating a cold solution of aniline sulphate (40 g. of aniline in 80 g. of sulphuric acid and 40 c.c. of water), with a solution of sodium nitrite (36 g.) in water (80 c.c.). The solution of diazo salt was then poured in small quantity with constant shaking to *o*-cresol (80 g.) heated to about 95°. A black oil separated and much nitrogen was evolved. The black oil was separated

and subjected to distillation in superhated steam and collected in four fractions:

(*i*) Temp. of the steam 120°, temp. of oil-bath containing the flask 115°—phenol and cresol.

(*ii*) Steam (150°), temp. of oil-bath (130°)—phenyl ether.

(*iii*) Steam (180°), temp. of oil-bath (160°)—mixture of the ethers and the diphenyl derivative,

(*iv*) Steam (200-220°), temp of oil-bath (190°)—pure diphenyl derivative.

The *4-hydroxy-3-methyldiphenyl* was separated from phenyl ether by caustic alkali, the undissolved ether was removed by means of ether and the alkali solution was acidified. The separated diphenyl derivative was dissolved in ether, ether distilled off and it was then crystallised from alcohol, m.p. 114°. (Found: C, 84·5; H, 6·4. $C_{13}H_{12}O$ requires C, 84·7 ; H, 6·50 per cent).

Methylation of 4-hydroxy-3-methyldiphenyl.—It was dissolved in 10 % alkali, and dimethylsulphate (slight excess over the calculated amount) was added in small portion with constant shaking, and the reaction was completed on the water-bath. The methoxy derivative was extracted with ether, ether distilled off and crystallised from alcohol, m.p. 76°. (Found: C, 84·6; H, 7·0. $C_{14}H_{14}O$ requires C, 84·8; H, 7·0 per cent).

Acetylation of 4-hydroxy-3-methyldiphenyl.—It was acetylated by refluxing for 3 hours with acetic anhydride in presence of a drop of pyridine. The reaction mixture was poured into water and the precipitate crystallised from alcohol, m.p. 83°. (Found: C, 79·0; H, 6·0. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·1 per cent).

Oxidation of 4-methoxy-3-methyldiphenyl.—A concentrated solution of permanganate (1·6 g.) was added gradually to a suspension of the substance (1 g.) in boiling water (10 c.c.). It was then allowed to reflux till the permanganate was decolourised (12 to 15 hours), filtered and acidified. It was finally crystallised from dilute acetic acid, m.p. 172°. (Found: C, 73·4; H, 5·0. $C_{14}H_{12}O_3$ requires C, 73·6; H, 5·2 per cent).

Decarboxylation of the acids.—The acid was heated with lime to 200° and the product was extracted with alcohol, from which on evaporation 4-methoxy- or 2-methoxydiphenyl crystallised out. Almost identical conditions and processes were employed in the preparation of the diphenyls and their derivatives, described in the following table.

	Amine and phenol.	Products.	Formulae.	M.p. or B.p.	Analytical data. Found.	Req.	Found.	Req.	Remarks.
1.	*o*-Toluidine + *o*-cresol	4-Hydroxy-3 : 2′-dimethyl diphenyl and 2 : 2′-Dimethylphenylether	$C_{14}H_{14}O$	160°/10 mm.	C, 84·6%	84·8%	H, 6·8%	7·0%	
	The *acetyl* derivative		$C_{16}H_{16}O_2$	130°/10 mm.	79·8	80·0	6·4	6·6	
	The *methoxy* derivative		$C_{15}H_{16}O$	125°/10 mm.	84·5	84·9	7·3	7·5	
	Oxidation product of methoxy derivative	4-Methoxy-3 : 2′-dicarboxydiphenyl	$C_{15}H_{12}O_5$	210°	65·8	66·1	4·2	4·4	On heating with lime-4-methoxy-diphenyl.
2.	*m*-Toluidine + *o*-cresol	4-Hydroxy-3 : 3′-dimethyl diphenyl and 2 : 3′-Dimethylphenyl ether	$C_{14}H_{14}O$	175°/9 mm.	84·7	84·8	7·0	7·0	
			$C_{14}H_{14}O$	170°/17 mm.	84·7	84·8	6·9	7·0	
	The *acetyl* derivative		$C_{16}H_{16}O_2$	158°/10 mm.	79·6	80·0	6·2	6·6	
	The *methoxy* derivative		$C_{15}H_{16}O$	150°/10 mm.	84·7	84·9	7·4	7·5	
	Oxidation product of methoxy derivative	4-Methoxy-3 : 3′-dicaboxydiphenyl	$C_{15}H_{12}O_5$	232°	66·0	66·1	4·1	4·4	On heating with lime 4-methoxy-diphenyl.
3.	*p*-Toludine and *o*-cresol	4-Hydroxy-3 : 4′-dimethyl-diphenyl and	$C_{14}H_{14}O$	136°	84·5%	84·8%	7·1%	7·0%	
		2 : 4′-Dimethylphenylether	$C_{14}H_{14}O$	180°/17 mm.	84·6	84·8	6·8	7·0	
	The *acetyl* derivative		$C_{16}H_{16}O_2$	74°	79·6	80·0	6·5	6·6	
	The *methoxy* derivative		$C_{15}H_{16}O$	80°	84·5	84·9	7·1	7·5	On heating with lime 4-methexy diphenyl.
	Oxidation product of methoxy derivative	4-Methoxy-3 : 4′-dicarboxydiphenyl	$C_{15}H_{12}O_5$	275°	65·7	66·1	4·2	4·4	

Amine and phenol.	Products.	Formulae.	M.p. or B.p.	Analytical data. Found.	Req.	Found.	Req.	Remarks.
4. Aniline and *m*-cresol	4-Hydroxy-2-methyldiphenyl and	$C_{13}H_{12}O$	180°/15 mm.	C, 84·5%	84·7%	H, 6·2%	6·5%	
	2-Methylphenylether							
The *acetyl* derivative		$C_{15}H_{14}O_2$	168°/12 mm.	79·4	79·6	6·1	6·1	
The *methoxy* derivative		$C_{14}H_{14}O$	164°/12 mm.	84·6	84·8	6·6	7·0	On heating with lime 4-methoxydiphenyl.
Oxidation product of methoxy derivative	4-Methoxy-2-carboxydiphenyl	$C_{14}H_{12}O_3$	135°	73·2	73·6	5·1	5·2	
5. *o*-Toluidine + *m*-cresol.	4-Hydroxy-2 :2′-dimethyldiphenyl and	$C_{14}H_{14}O$	185°/15 mm.	84·4	84·8	6·9	7·0	
	2 : 3′-Dimethylphenyl ether.	$C_{14}H_{14}O$	170°/17mm.	84·7	84·8	6·9	7·0	
The *acetyl* derivative.	.....	$C_{16}H_{16}O_2$	175°/12 mm.	79·5	80	6·3	6·6	
The *methoxy* derivative.	.....	$C_{15}H_{16}O$	170°/15 mm.	84·6	84·9	7·3	7·5	
Oxidation product of methoxy derivative,	4-Methoxy-2 :2′-dicarboxydiphenyl.	$C_{15}H_{12}O_5$	210°	65·6	66·1	4·0	4·4	On heating with lime 4-methoxydiphenyl.
6. *m*-Toluidine + *m*-cresol.	4-Hydroxy-2 :3′-dimethyldiphenyl and	$C_{14}H_{14}O$	195°/15 mm.	84·6	84·8	6·6	7·0	
	3 :3′-Dimethyldiphenylether							
The *acetyl* derivative.	.....	$C_{16}H_{16}O_2$	186°/15 mm.	79·7	80·0	6·9	6·6	

Amine and phenol.	Products.	Formulae.	M.p. or B.p.	Analytical data. Found.	Req.	Found.	Req.	Remarks.
The *methoxy* derivative.	.....	$C_{15}H_{16}O$	185°/15 mm.	C, 84·7%	84·9%	H, 7·2%	7·5%	
Oxidation product of methoxy derivative.	4-Methoxy-2 :3′-dicarboxydiphenyl	$C_{15}H_{12}O_5$	240°	66·0	66·4	4·4	4·4	On heating with lime 4-methoxydiphenyl.
7. *p*-Toluidine and *m*-cresol.	4-Hydroxy-2 :4′dimethyldiphenyl and	$C_{14}H_{14}O$	225°/15 mm.	84·7	84·8	6·8	7·0	
	4′: 3-Dimethylphenylether	$C_{14}H_{14}O$	175°/17 mm.	84·8	84·8	6·7	7·0	
The *acetyl* derivative.	.....	$C_{16}H_{16}O_2$	210°/15 mm.	79·6	80·0	6·5	6·6	
The *methoxy* derivative.	.....	$C_{15}H_{16}O$	205°/13 mm.	84·8	84·9	7·5	7·5	
Oxidation product of methoxy derivative.	4-Methoxy-2 :4′-dicarboxydiphenyl	$C_{15}H_{12}O_5$	280°	65·9	66·1	4·1	4·4	On heating with lime 4-methoxydiphenyl.
8. *o*-Toluidine and *p*-cresol.	2-Hydroxy 2′ :5-dimethyldiphenyl and	$C_{14}H_{14}O$	195°/14 mm.	84·6	84·8	7·0	7·0	
	4′ :2-Dimethylphenylether	$C_{14}H_{14}O$	180°/17 mm.	84·6	84·8	6·8	7·0	
The *acetyl* derivative.	.....	$C_{16}H_{16}O_2$	186°/10 mm.	79·7	80·0	6·3	6·6	
The *methoxy* derivative.	.....	$C_{15}H_{16}O$	185°/13 mm.	84·5	84·9	7·2	7·5	
Oxidation product of methoxy derivative.	2-Methoxy-5 :2′-dicarboxydiphenyl	$C_{15}H_{12}O$	Does not melt below 300°.	65·9	66·1	4·3	4·4	On heating with lime 2-methoxydiphenyl.

Amine and phenol.	Products.	Formulae.	M.p. or B.p.	Analytical data. Found.	Req.	Found.	Req.	Remarks.
9- *m*-Toluidine and *p*-cresol.	2-Hydroxy-5 :3′-dimethyldiphenyl and	$C_{14}H_{14}O$	210°/14 mm.	C, 84·6%	84·8%	H, 6·9%	7·0%	
	4′ :3-Dimethylphenylether	$C_{14}H_{14}O$	175°/17 mm.	84·5	84·8	6·7	6·7	
The *acetyl* derivative.	.....	$C_{16}H_{16}O_2$	204°/15 mm.	80·1	80·0	6·4	6·6	
The *methoxy* derivative.	... ..	$C_{15}H_{16}O$	200°/13 mm.	84·7	84·9	7·3	7·5	
Oxidation product of methoxy derivative.	2-Methoxy-5 :3′-dicarboxydiphenyl	$C_{15}H_{12}O_5$	Does not melt below 300°	65·9	66·1	4·2	4·4	On heating with lime 2-methoxydiphenyl.
10. *p*-Toluidine and *p*-cresol.	2-Hydroxy-5 :4′-dimethyldiphenyl	$C_{14}H_{14}O$	225°/15 mm.	84·5	84·8	7·2	7·0	
	4 :4′-Dimethylphenylether							
The *acetyl* derivative.	.....	$C_{16}H_{16}O_2$	215°/15 mm.	79·9	80·0	6·6	6·6	
The *methoxy* darivative.	.....	$C_{15}H_{16}O$	205/42 mm.	84·5	84·9	7·9	7·5	
Oxidation product of methoxy derivative.	2-Methoxy-5 :4′-dicarboxydiphenyl	$C_{15}H_{12}O_5$	Does not melt below 300°.	65·8	66·1	4·1	4·4	On heating with lime 2-methoxydiphenyl.

In conclusion, the author desires to express his thanks to Prof. Dr. P. C. Mitter for much encouragement and valuable advice during the course of this work.

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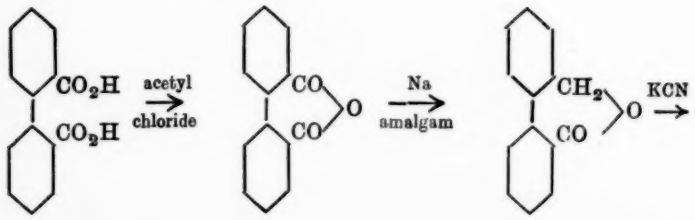
Studies in Diphenyl Series. Part II. A New Method of the Synthesis of 9-Hydroxyphenanthrene.

By Nripendranath Chatterjee.

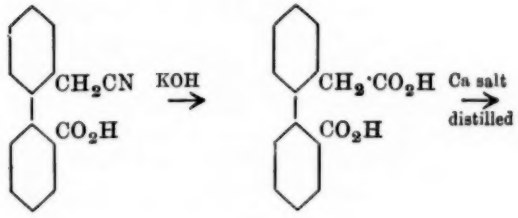
From the point of view of constitution, phenanthrene is intimately related to naphthalene on the one hand and diphenyl on the other, so phenanthrene or its derivatives may be synthesised from the derivatives of both.

Confining our attention to the syntheses in which the starting materials are derivatives of diphenyl it may be observed that the methods available so far are of limited scopes (*cf.* Graebe and Aubin, *Annalen*, 1888, **247**, 257; Libermann, *Ber.*, 1911, **44**, 1453; Kenner and Turner, *J. Chem. Soc.*, 1911, **99**, 2101).

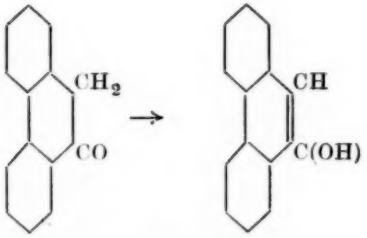
The method described in the present investigation is one capable of considerable extension. The starting material is *oo'*-diphenic acid or a derivative of the substance. *o-o'*-Diphenic acid is converted to the anhydride (I) by acetyl chloride and reduced by sodium amalgam (5%). The lactone of 2'-oxymethyl-2 carboxydiphenyl (II) which is formed is heated with KCN at 180°-190° for 3 to 4 hours when due to the ring opening, the potassium salt of 2-cyanomethyl-2-carboxydiphenyl (III) is obtained. The above compound when boiled with 30% KOH yields 2-carboxymethyl-2-carboxydiphenyl (IV). It is converted to the corresponding calcium salt which on dry distillation yields 9-hydroxyphenanthrene (V). From the reaction product the compound is isolated by extracting with alcohol and precipitating it as the picrate.



(I) (II)



(III) (IV)



(V)

In practice one of the greatest difficulties to be encountered is with respect to the properties of the lactone. The yield of the lactone is not satisfactory, since due to a secondary reaction the anhydride itself is converted into diphenic acid and its mono ester, But this does not in any way interfere with the processes involved. The acid, thus produced, as well as the mono ester (after its hydrolysis) can be used over and over again, and there is little loss of material.

With substituted *oo'*-diphenic acids, the corresponding phenanthrene derivatives may be obtained and there will be no ambiguity due to the orientation of the various groups.

Experimental.

Lactone of 2-hydroxymethyl-2-carboxydiphenyl (II).—Sodium amalgam (5%) was added in portions during 24 hours to a solution of diphenic anhydride (40 g.) in alcohol (100 c. c) which was mechanically stirred. The solution was kept acidic by means of dilute sulphuric acid (excess of acid must be avoided, otherwise too much of ester will be formed). The solution was made alkaline and the sodium sulphate was filtered and the alkaline filtrate after dilution was

a solution of the free acid, the mono acid ester and the lactone and they were separated thus: (*i*) Fractional precipitation by the addition of regulated quantities of acid. (*ii*) Extraction with dilute $NaHCO_3$ solution which dissolves most of the mono ester. (*iii*) Fractional crystallisation from ethereal solution. It has been thus possible to obtain the pure lactone free from the acid and the mono-ester. It crystallises from benzene in needles, m.p. 186°, yield 5-6%. This lactone has been prepared by Kenner and Turner, (*loc. cit.*) (Found: C, 79·9; H. 4·7. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·7 per cent).

2′-Cyanomethyl-2-carboxydiphenyl (III).—The lactone (0·5 g.) was well mixed with potassium cyanide (E.P, 0·3g.) and heated in a test tube in an oil-bath for 3 to 4 hours. The resulting dark coloured cold mass was digested with water and the insoluble portion removed by extraction with ether. The aqueous layer was filtered and on acidification the free acid was precipitated. It crystallises from benzene in light brown needles, m. p. 240°. (Found: N, 5·7. $C_{15}H_{11}O_2N$ requires N, 5·9 per cent).

2′-Carboxymethyl-2-carboxydiphenyl (IV).—2′-Cyanomethyl-2-carboxydiphenyl was dissolved in 30% caustic potash solution and allowed to boil till no more ammonia was evolved. It was then filtered and acidified, when 2′-carboxymethyl-2-carboxydiphenyl separated, m. p. 295°. (Found: C, 70·0; H, 4·4. $C_{15}H_{12}O_9$ requires C, 70·3; H, 4·6 per cent).

9-Hydroxyphenanthrene (V).—The calcium salt of (IV) was placed in a small pyrex retort glass to the stem of which was attached a wide mouth test tube with a side tube which can be connected to a vacuum pump. The bulb was now rapidly heated when a yellow oil condensed in the test tube. The distillate was dissolved in alcohol and on addition of a saturated solution of picric acid a red coloured picrate was precipitated. It was filtered, washed and recrystallised from alcohol, m.p. 185°. 9-Hydroxyphenanthrene, regenerated from the pure picrate, melts at 153°.

In conclusion, the author desires to express his thanks to Professor Dr. P. C. Mitter for much encouragement and advice during the course of this work.

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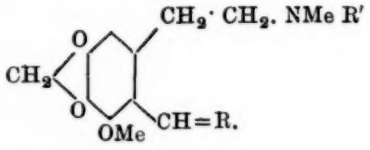
Studies in the Cotarnine Series. Part II. The Reactivity of the Aldehyde Group in Cotarnine and Benzoyl Cotarnines.

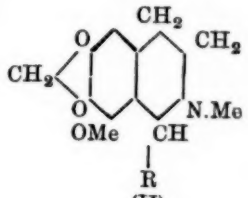
By B. B. Dey and (Miss.) P. Lakshmi Kantam.

The reactions of cotarnine with phenyl *iso*cyanate and phenyl *iso*thiocyanate studied in Part I (*J. Indian Chem. Soc.*, 1934, **12**, 835), depended on the activity of the secondary imino-hydrogen atom in cotarnine and thereby furnished evidence of the aldehydic structure for this base. We have now examined such reactions of cotarnine as involve the activity of the aldehyde group.

Cotarnine reacts smoothly with hydroxylamine yielding a crystalline derivative which should be considered to have the structure of an oxime (I, R′=H ; R=NOH), but may also be supposed to be derived from the tetrahydro-*iso*quinoline or carbinol form (II, R=NHOH)



(I)



(II)

The product readily yields di-acyl derivatives and interacts smoothly with two molecules of phenyl *iso*cyanate, the resulting compound being identified with the product synthesised from cotarnomethylphenylurea oxime and phenyl *iso*cyanate (*loc. cit.*). These reactions clearly indicate the simultaneous presence of the oximino-hydroxyl group and of the secondary imino-hydrogen atom in cotarnine oxime and thus rule out Formula II. Again on reducing the oxime with sodium and alcohol, ammonia was found to be evolved and the product was identified as hydrocotarnine by the usual tests. This reaction can be easily understood if we assume that the reduction of the oxime to the amine is followed by the

elimination of ammonia from the amino and the secondary imino-groups and the consequent closure of the *iso*quinoline ring.

Further evidence of the activity of the aldehyde group of cotarnine is afforded by the ease with which this base condenses with aromatic amines such as aniline (Freund, *Ber.*, 1903, **36**, 1528) and the toluidines, anils being formed (I, R=NPh; R′=H).

These compounds are unstable and are decomposed quickly by alkalis, but they dissolve unchanged in cold acids and are recovered on basification. Attempts to prepare the benzoyl derivative of cotarno-*p*-toluidil with a view to identify it with the product obtained by the condensation of *p*-toluidine with benzo-cotarnine resulted in the production only of benzo-*p*-toluidide (m. p. 158°).

The reactions of cotarnine with benzoyl chloride (Roser, *Annalen*, 1889, **254**, 335) and with *o*-nitrobenzoyl chloride lend further support to the open chain aldehyde-imine structure. Of the two possible structures (I, R=O; R′=CO·Ph.; II, R=O·CO·Ph) for the benzoylated product, Formula III has obviously to be accepted as correct on the following grounds:—

(*a*) It is quite insoluble in dilute acids showing that the neutralisation of the basic N· Me group by the benzoyl radical has taken place.

(*b*) It readily forms a crystalline monoxime which is soluble in cold alkali and which yields monoacetyl and monobenzoyl derivatives insoluble in cold alkali. The benzoyl derivative is found to be identical with the product of benzoylation of cotarnine oxime.

(*c*) It is oxidised by alkaline permanganate to benzoyl cotarninic acid.

(*d*) It condenses with aromatic amines with extreme ease yielding remarkably stable anils and toluidils (I, R′=CO·Ph; R=NPh).

The stability of these compounds as well as of the anils and toluidils derived from cotarnomethyl phenyl urea is in striking contrast with the instability of the corresponding derivatives of cotarnine itself, and the difference should obviously be attributed to the presence of the mobile imino-hydrogen atom in the latter and its absence in the former. Once this hydrogen is removed and the basic function of cotarnine depressed either by acylation or by quarternary salt formation, the aldehydic group in the molecule seems to be released from its peculiar condition of bondage to the NH-group, resuming its activity and yielding the usual stable derivatives. The presence of the secondary imino-hydrogen in cotarnine and its absence in benzoyl

cotarnine and cotarnomethylphenylurea would thus account for the remarkable difference in the reactivity of the aldehydic group which is present in both these compounds.

The condensation of cotarnine with *o*-nitrobenzoyl chloride under the usual conditions gave *o*-nitrobenzoyl cotarnine (I, R=O ; R′=*o*-$NO_2 \cdot C_6H_4CO$) in excellent yield. In view of the proximity of the nitro- and the aldehyde groups in the molecule of this compoud it was considered possible that the reduction of the nitro group would lead to the syntheses of interesting compounds and the subject is still under investigation.

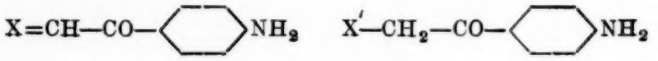
Notwithstanding this accumulation of positive evidence of the occurrence of a reactive aldehyde group in the acylated derivatives of cotarnine, it has been observed that the latter do not enter into reaction with many compounds with which the aldehyde group of cotarnine itself condenses freely. Thus benzoylcotarnine does not condense with compounds containing reactive methylene groups such as resorcinol, phloroglucinol, malonic ester, nitromethane, etc., with which cotarnine easily reacts. Indeed, the condensation with nitromethane is quantitative and occurs so readily that it may serve as an excellent test for detecting traces of cotarnine. It is very probable that condensations of the latter type occur only with the carbinol form of cotarnine, the unreactivity of benzoyl cotarnine being explained by the impossibility of the formation of the carbinol phase in the latter. The acceptance of this view becomes all the easier when it is borne in mind that such condensations as those mentioned above are usually carried out in the presence of alcohol, a reagent which has been definitely shown to favour the change of the aldehydic into the carbinol form.

It will be seen that two structures are possible for the products of condensation of cotarnine with such compounds as acetone, acetophenone, *p*-aminoacetophenone, urea, phthalimidine, resorcinol and its monomethyl ether, nitroresorcinol, aromatic nitro-aldehydes, etc., all of which have been examined by us. They should be represented either as derivatives of 1-β-*N*-methyl-aminoethyl-2-benzaldehyde, if the cotarnine reacted in the aldehydic form, or as 1-substituted *N*-methyltetrahydro*iso*quinoline derivatives, the cotarnine reacting in the carbinol form:

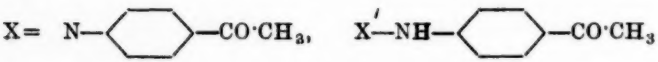
Liebermann and Glawe (*Ber.*, 1904, **37**, 211 2738) observed that a discrimination between the two structures might be made by such reactions as methylation or acetylation indicative of the presence or

absence of a hydrogen atom attached to the nitrogen. Attempts made by us to prepare such derivatives, however, have resulted either in the decomposition of the compounds into their respective components, *e.g.*, with anhydrocotarnino-carbamide and anhydrocotarnino-phthalimidine, or in the recovery of the original products. Anhydrocotarnino-*p*-amidoacetophenone provided the only exception in which a mono-acetyl derivative soluble in dilute acids was obtained by acetylation.

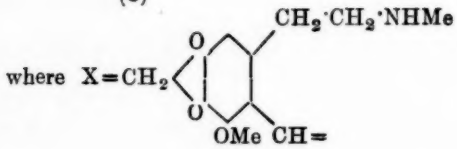
The condensation of cotarnine with *p*-amidoacetophenone may be expected to yield products having the following constitutions:—

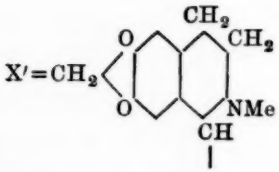


(A) (B)



(C) (D)





The product was found to contain a free diazotisable aminogroup so that formulæ C and D have to be rejected. On treating with excess of acetic anhydride it formed only a monoacetyl derivative which dissolved readily in cold dilute acids. This clearly points to structure B as the correct one since a compound of Formula A should be expected to yield a diacetyl derivative insoluble in dilute acids. The general trend of the evidence obtained so far seems, therefore, to be in favour of regarding these products as 1-substituted tetrahydro-*iso*quinoline derivatives.

Experimental.

Action of hydroxylamine hydrochloride on cotarnine: *Cotarnine oxime* (Roser, *Annalen*, 1889, **253**, 335).—Roser refluxed the cotarnine solution with hydroxylamine for several hours. This we find to be unnecessary as the formation of the oxime takes place even in the cold. Cotarnine (2 g.) was suspended in water (20 c.c.), a solution of hydroxylamine hydrochloride (1 g.) and sodium acetate crystals (2 g.) added and warmed on the water-bath when a clear solution was obtained. This was evaporated to about half the volume on the water-bath, cooled, and made alkaline with sodium carbonate and allowed to stand, when the oxime separated out almost quantitatively. Crystallisation from alcohol gave colourless rectangular plates, m.p. 157° (m.p. recorded in literature is 165-68°). The oxime dissolved in dilute alkali on warming slightly and was recovered on neutralising the liquid.

Phenylurethane of cotarnomethylphenylurea oxime.—Cotarnine oxime was suspended in dry benzene and treated slowly with the calculated amount of phenyl *iso*cyanate. The oxime dissolved with evolution of heat and the product crystallised in the course of a few seconds, m.p. 151°, yield quantitative. It was identified with the compound obtained by the action of phenyl *iso*cyanate on cotarnomethylphenylurea oxime (*loc. cit.* p. 840).

Cotarnomethylphenylthiourea oxime was prepared as above by the action of phenyl *iso*thiocyanate on cotarnine oxime, the benzene solution being warmed on the water-bath for a few minutes. The product, m.p. 142°, was identified with the compound obtained by the oximation of cotarnomethyl phenyl thiourea (*loc. cit.* p. 842). As we have observed before, the phenyl *iso*thiocyanate does not react with the oximino-hydroxyl group.

Benzoylated oxime of benzoyl cotarnine.—Cotarnine oxime (1·6 g.) was triturated in a mortar with 40 c.c. of *N*-NaOH and the opalescent solution treated in the cold with 2 c.c. of benzoyl chloride and vigorously shaken. The separated solid melted rather indefinitely (140°-50°). Two crystallisations from dilute alcohol gave colourless woolly fibres, m.p. 158°, quite insoluble in alkali. Admixture with benzoyl cotarnine oxime (m.p. 165°) depressed the m.p. to 140°. (Found: C, 67·55; H, 5·32; N, 6·6. $C_{26}H_{24}C_6N_2$ requires C, 67·82; H, 5·22; N, 6·1 per cent).

Acetylated oxime of acetylcotarnine.—Cotarnine oxime (1 g.) was treated with 10 drops of acetic anhydride, gently warmed and allowed

to stand for half an hour. It was then poured into water, the precipitate collected, washed and crystallised twice from dilute alcohol as soft colourless threads, m.p. 113°, insoluble in alkali. (Found: N, 8·51. $C_{16}H_{20}O_6N_2$ requires N, 8·33 per cent).

Reduction of Cotarnine Oxime to Hydrocotarnine

Cotarnine oxime (1 g.) was heated under reflux with absolute alcohol (30 c.c.) and sodium (2 g.) added in small pieces during one hour. Ammonia was copiously evolved and at the end of the reaction, the alcohol was mostly boiled off, water added and the oily product extracted repeatedly with ether. The thick reddish oil after distilling off the ether did not solidify easily. It was rubbed with a few drops of HBr solution when crystals of the hydrobromide of the base separated out. The salt was dissolved in the minimum quantity of water, basified strongly with caustic soda and cooled in ice when the hydrocotarnine separated out as colourless needles, m.p. 54°; the hydrobromide (m.p. 224°) and the picrate (m.p. 173°) were prepared and identified with the hydrobromide and picrate of an authentic specimen of hydrocotarnine. The platinichloride of the base was analysed. [Found: Pt, 23·04. $(C_{12}H_{15}O_3N, HCl)_2$ Pt Cl_4 requires Pt, 22·9 per cent).

Condensation of Cotarnine with Aromatic Amines.

Cotarnine anil (Freund and Becker, *Ber.*, 1903, **36**, 1527) has been prepared in quantitative yield by simply rubbing together molecular quantities of cotarnine (2 g.) and freshly distilled aniline (0·8 g.) in a mortar with a few drops of water. The oil solidified after some time. On washing with water containing a little hydrochloric acid it formed a colourless crystalline mass, m.p. 120°. (Found: N, 9·12. $C_{18}H_{20}O_3N_2$ requires N, 8·97 per cent).

Cotarnino-p-toluidil, m.p. 114-115°, was prepared in the same way. Attempt to crystallise it from hot alcohol led to decomposition into the components. Similarly on attempting the benzoylation of the product under the usual conditions, needles, m.p. 158°, identical with benzo-*p*-toluidide, were obtained. (Found: N, 8·51 $C_{19}H_{22}O_3N_2$ requires N, 8·59 per cent) *Cotarnino-o-toluidil*, prepared in the same way, melted at 119°.

Benzoyl cotarnine was obtained by an improvement of the process described by Roser (*loc. cit.*). Cotarnine (2 g.) was triturated with *N*-alkali (20 c.c.) and benzoyl chloride (1 c.c.) in a mortar for 15

minutes when the oil solidified. The strongly alkaline solution was poured off, the solid rubbed well with water and dilute hydrochloric acid and then crystallised from hot alcohol as colourless prisms, m.p. 124°, yield quantitative. The product is very stable and is not attacked by dilute acids or alkalis even on warming.

Benzoyl cotarnine oxime was prepared in quantitative yield by mixing a hot alcoholic solution of benzoyl cotarnine (1 g.) with a concentrated aqueous solution of hydroxylamine hydrochloride (0·58 g.) and sodium acetate (1 g.). Colourless needles, m.p. 165°. On treating this with benzoyl chloride, the same product (m.p. 158°) as that formed by the benzoylation of cotarnine oxime was obtained.

The acetyl derivative of benzoyl cotarnine oxime was very easily prepared by the acetylation of the oxime in the usual way. It separated from alcohol in masses of soft threads, m.p. 152°. (Found: C, 63·1; H, 5·7; N, 7·3. $C_{21}H_{22}O_6N_2$ requires C, 63·31; H, 5·53; N, 7·04 per cent).

Benzoyl cotarnine azine, prepared in the usual way with hydrazine hydrochloride and alkali, crystallised from acetic acid in diamond shaped plates, m.p. 220°. (Found: N, 8·37. $C_{38}H_{38}O_8N_4$ requires N, 8·26 per cent).

Oxidation of benzoylcotarnine to benzoylcotarninic acid.—Finely powdered benzoyl cotarnine (1 g.), suspended in a solution of sodium hydroxide (2 g. in 50 c.c. of water) was refluxed with a 4% solution of potassium permanganate (0·308 g. in 8 c.c. of water) which was added slowly during half an hour. On cooling the filtrate some unchanged benzoyl cotarnine crystallised out. The yellow filtrate was saturated with sulphur dioxide, extracted thrice with ether and the white solid left on evaporation of the ether crystallised from dilute acetic acid. It formed a microcrystalline powder, m.p. 156°, dissolving in cold dilute sodium carbonate to a clear solution. The silver salt which was thrown down as a pale yellow precipitate from neutral solutions, was analysed. (Found: Ag, 22·9. $C_{19}H_{18}O_6NAg$ requires Ag, 23·2 per cent).

Benzoyl cotarnine anil, prepared by Freund and Becker (*loc. cit.*), was obtained in an yield of 1·2 g. from 1 g. of cotarnine by rubbing the two bases with a little water and working up the resulting solid in the usual way. It was very stable and crystallised from boiling alcohol in small needles, m.p. 164°.

Benzoyl cotarnine-o-toluidil crystallised from alcohol in soft colourless needles, m. p. 150°. (Found: N, 6·5. $C_{26}H_{26}O_4N_2$ requires N, 6·5 per cent).

The m-*toluidil* and p-*toluidil* of benzoyl cotarnine, prepared by the same method, melted at 113° and 111° respectively. *Benzoyl cotarnine*-p-*phenetidil* was prepared by rubbing together benzoyl cotarnine (1 g.) with 10-12 drops of *p*-phenetidine, adding 4 c.c. of water and treating the separating oil with a few drops of dilute acetic acid, and crystallising the resulting solid from boiling alcohol. It separated in stellate clusters of needles, m. p. 135°. (Found: N, 5·83. $C_{27}H_{28}O_5N_2$ requires N, 6·08 per cent).

o-*Nitrobenzoyl cotarnine* was prepared from cotarnine and freshly prepared *o*-nitrobenzoylchloride by the same method as that used in preparing benzoyl cotarnine. It formed small prisms melting at 138°, sparingly soluble in alcohol and insoluble in acids and alkali. (Found: C, 58·6; H, 4·5 ; N, 7·31. $C_{19}H_{18}O_7N_2$ requires C, 59·06; H, 4·66; N, 7·25 per cent).

o-*Nitrobenzoyl cotarnine oxime* was prepared by suspending the nitrobenzoyl cotarnine (1 g.) in alcohol (6 c.c.) and adding a solution of hydroxylamine hydrochloride (0·5 g.) and sodium acetate (1 g.) in the minimum amount of water. On warming, a clear solution resulted and this was soon followed by the separation of slightly yellow prismatic needles, m. p. 193-94°; yield quantitative. (Found: N, 10·35. $C_{19}H_{19}O_7N_3$ requires N, 10·47 per cent).

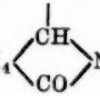
o-*Nitrobenzoyl cotarnine anil* was prepared by rubbing aniline and the cotarnine in the usual way and then adding a few drops of dilute acetic acid. It was crystallised from a mixture of benzene and petroleum as small plates, m. p. 164°. It is very sparingly soluble in in alcohol. (Found: N, 9·12. $C_{25}H_{23}O_6N_3$ requires N, 9·11 per cent).

Anhydrocotarnino-p-*amido-acetophenone* crystallised out on warming a solution of cotarnine (1 g.) and *p*-amido-acetophenone (0·6 g.) in absolute alcohol (12 c. c.) on the water-bath to 40° for 15 minutes and leaving overnight, m. p. 190-91°; yield 1·2 g. It is very sparingly soluble in the usual organic solvents but dissolves instantly in dilute acids and is reprecipitated on basification. (Found: C, 66·93; H, 6·25. $C_{20}H_{22}O_4N_2$ requires C, 67·79; H, 6·22 per cent).

The *monoacetyl* derivative, prepared in the usual way, crystallised in small needles, m. p. 105°. It dissolved unchanged in dilute acids to form a yellow solution. (Found: N, 7·29. $C_{22}H_{24}O_5N_2$ requires N, 7·07 per cent).

Anhydrocotarnino-carbamide (II, R=NHCONH$_2$).—Pure cotarnine (10 g.) was dissolved in absolute alcohol (60 c.c.) by gently warming and a solution of urea (2·8 g.) in the same solvent (50 c.c.) added

and the clear solution warmed on the water-bath for half an hour at a temperature not exceeding 45°. The urea derivative separated almost immediately on cooling as colourless prisms which were collected after an hour, washed with cold alcohol and dried; m. p. 182°, yield 11 g. The substance was insoluble in cold alcohol, ether, benzene, etc.; it dissolved in hot water but did not crystallise on cooling as it underwent considerable decomposition during the process. When a hot aqueous solution of the substance was treated with picric acid, cotarnine picrate (needles, m. p. 143°) crystallised out. A cold aqueous solution was found to have a p_H of 7·7, *i.e.*, it was definitely alkaline. It dissolved instantly in cold dilute hydrochloric acid to a pale yellow solution and was recovered unchanged on basification after an hour. (Found: C, 55·3; H, 6·3. $C_{13}H_{17}O_4N_3$ requires C, 55·9; H, 6·1 per cent).

Anhydro-cotarninophthalimidine [II, R=C_6H_4 ] was

prepared in the same way as the urea compound, but the solid separated only on diluting the solution with water. It melted at 143-44° and was decomposed by boiling water. Cold dilute acids dissolved the substance unchanged. (Found: C, 67·77; H, 5·71, N, 8·13. $C_{20}H_{20}O_4N_2$ requires C, 68·19; H, 5·68; N, 7·95 per cent).

Anhydrocotarnino-resorcinol monomethyl ether separated as a cream coloured micro-crystalline powder, m. p. 221-22°, on warming the components in alcoholic solution to 40° and leaving overnight, yield quantitative. It is insoluble in ether and benzene, sparingly soluble in alcohol and very easily soluble in dilute acids. (Found: N, 4·27. $C_{19}H_{21}O_5N$ requires N, 4·08 per cent).

The condensations of cotarnine with the cresols (*o*-, *m*- and *p*-) and the naphthols (α- and β-) were tried without success.

Anhydrocotarnino-2-nitro-resorcinol, prepared in the same way from cotarnine and 2-nitroresorcinol crystallised in fine orange-coloured needles, m. p. 201°. Its properties were similar to those of the previous compound. It dissolved in cold hydrochloric acid and the sparingly soluble hydrochloride separated out almost immediately. (Found: N, 7·35. $C_{18}H_{18}O_7N_2$ requires N, 7·49 per cent. Found: Cl, 8·3. $C_{18}H_{18}O_7N_2$, HCl requires Cl, 8·6 per cent).

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Studies in the Cotarnine Series. Part III. Isomeric *bis*-Cotarnino-acetones.

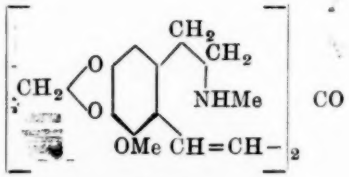
By B. B. Dey and (Miss) P. Lakshmi Kantam.

It has been explained in the previous papers that two structures are possible for the products of condensation of cotarnine with compounds containing the reactive methylene group, such as acetone, acetophenone, etc., according as they are viewed as derivatives of the aldehyde or the carbinol forms in the tautomeric system of which cotarnine is composed. Although all attempts to prepare such derivatives of these compounds as would furnish clear proofs of one structure or the other had hitherto failed or led to inconclusive results, the reinvestigation of the condensation of cotarnine and acetone which was originally studied by Liebermann and Kropf (*Ber.*, 1904, **37**, 211) has led to very interesting results and enabled us to isolate both the possible isomeric forms.

Liebermann condensed cotarnine with acetone using sodium carbonate as the condensing agent but no solvent, and obtained a crystalline product (m.p. 83°), of which the hydrochloride (m.p. 171°), the benzoyl derivative(m.p. 124°), and the met hiodide designated by him 'anhydromethyl cotarnino-acetone methylate' (m.p. 144°), were prepared. We have been able to confirm these observations except with regard to the methiodide, which is found to melt at 168° and from which a nitrogen-free product, *bis*-cotarnonideneacetone (VI) has been prepared in a somewhat impure condition by steaming its mixture with alkali.

Liebermann assumed that in this reaction one molecule each of cotarnine and acetone had condensed and that it might be a derivative of the aldehyde or the carbinol form.

Careful analyses and determinations of molecular weight have shown, however, that the product should be regarded as dicotarnylideneacetone (I), two molecules of cotarnine having reacted with one molecule of acetone:

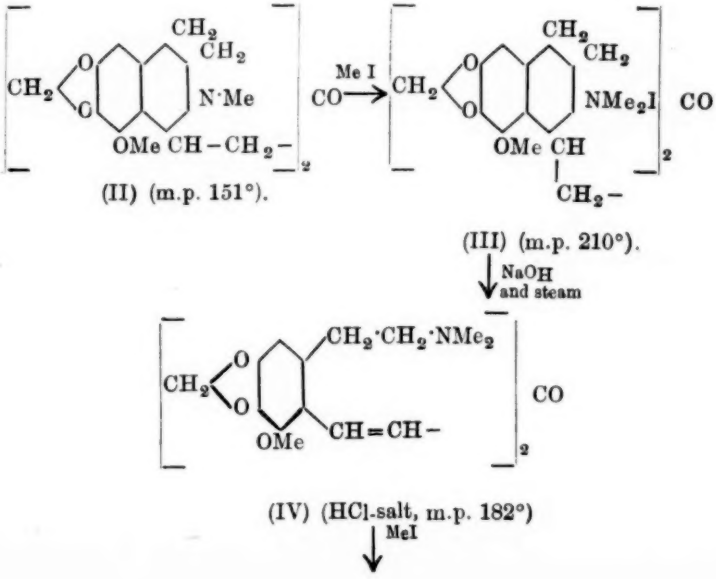


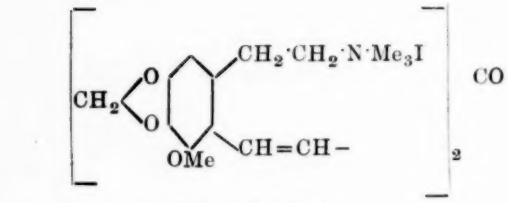
(I)

This is in agreement with the observations made by Pyman (*J. Chem. Soc.*, 1909, **93**, 1268, 1740) who obtained a similar product by condensing acetone with the aldehyde prepared from laudanosine by oxidation with manganese dioxide and sulphuric acid.

The significant observation has now been made by us that if this condensation with acetone be effected *in presence of alcohol* using, as before, sodium carbonate solution as the condensing agent, an entirely different but isomeric product (II) melting at 150-51° is obtained. The latter compound dissolves in dilute acids without any decomposition but is not acted upon by acetic anhydride, benzoyl chloride or phenyl *iso*cyanate. The absence of the secondary imino-group is thus indicated. It forms a different methiodide (III) m.p. 210°, which, on treatment with alkali and steaming, gives *N*-methyldicotarnylideneacetone (IV). The latter compound reacted with fresh methyl iodide, the resulting methiodide (V, m.p. 168°) being found to be identical with Liebermann's 'anhydromethylcotarninoacetone methylate' and to yield with alkali the same nitrogen-free product (II).

The new product (m.p. 151°) should evidently be assigned, therefore, the cyclic constitution (IV).



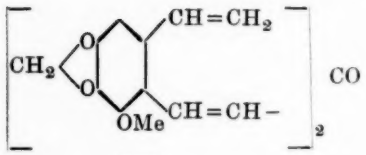


(V) (m.p. 168°)

NaOH and steam

MeI

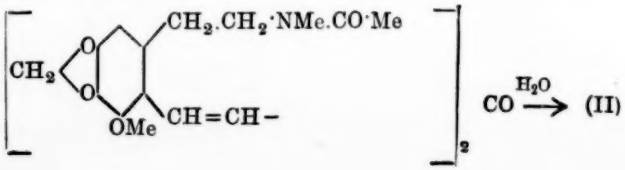
(I)



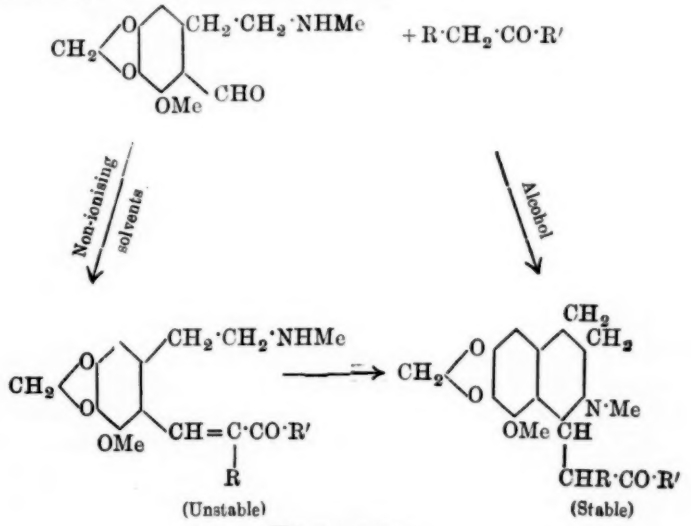
(VI)

It would be seen, therefore, that in the case of acetone two isomeric compounds (I) and (II) may be obtained by working under different conditions. The view that the change of the aldehyde into the carbinol phase has been effected by the solvent is strikingly supported by the observation that the unsaturated compound (I), m.p. 83°, is rapidly and *quantitatively* converted into the saturated one (II), m.p. 151°, by crystallisation from hot alcohol.

Several attempts made to differentiate between the two isomers in the case of the other condensation products, *e.g.* with acetophenone, etc., have hitherto been unsuccessful, the stable *iso*quinoline derivative being the only recognisable product of the reaction. This is undoubtedly due to the remarkable tendency of the iminohydrogen to migrate to the aldehydic carbon atom, any attempts at preparing derivatives resulting in the closure of the *iso*quinoline ring. Thus Liebermann's compound (m.p. 83°), on treatment with cold acetic anhydride, is found to be converted not into the expected acetyl derivative, but into the isomer (m.p. 151°). The reaction is best explained by assuming the formation of an intermediate acetyl compound which is immediately hydrolysed by water as follows:—



The acceptance of these views would make the mechanism of the reaction of cotarnine with compounds of the type of resorcinol in which the keto-enol change is known to occur so readily and also with other compounds containing reactive methylene groups, at once intelligible. The condensation, if effected in the presence of non-ionising solvents, *e.g.*, benzene, is assumed to occur with the aldehyde group, but in most cases the mobility of the imino-hydrogen atom causes the intermediate unsaturated products to be so unstable that ring-closure follows almost immediately with the formation of *N*-methyl tetrahydro-*iso*quinoline derivatives. The case of the acetone condensation product provides the only exception in which the unsaturated compound is found to be sufficiently stable to permit of its isolation and study. The following scheme should, therefore, represent the course of all condensations of this type occurring between ketomethylene compounds and cotarnine:—



EXPERIMENTAL.

bis-*Cotarninoacetone* (II).—Cotarnine (5 g.) and acetone (2 c.c.) were mixed with 25 c. c. of absolute alcohol, a small amount of anhydrous sodium carbonate added and the clear solution kept at laboratory temperature for 2 days. On pouring the liquid into water an oil was precipitated which, on rubbing and keeping in contact with water for 24 hours, completely solidified. It was dissolved in dilute hydrochloric acid, reprecipitated with ammonia and then crystallised from hot dilute alcohol as colourless crystals, m. p. 150-51°, yield 3·5 g.

It dissolved in cold acetone and benzene but more sparingly in alcohol. A sparingly soluble hydrochloride separated from its solution in cold 4 *N*-HCl, m. p. 167° (decomp.) [Found: C, 64·77; H, 6·5; N, 5·19; M. W. (ebulliscopic in acetone), 516. $C_{27}H_{32}O_7N_2$ requires C, 65·32; H, 6·45; N, 5·62 per cent. M. W. 496]. (Found: Cl, 11·98. $C_{27}H_{32}O_7N_2$, 2 HCl requires Cl, 12·50 per cent).

bis-*Cotarninoisopropyl alcohol.*—The previous compound (1 g.) was dissolved in a slight excess of dilute hydrochloric acid and the calculated amount of freshly prepared sodium amalgam (2·5%) was added in small quantities at a time. The mixture was shaken well and left overnight. The clear supernatant solution was then decanted from the mercury and basified with 2% alkali when the product separated as an oil which quickly solidified. It was washed with water and purified by dissolving in dilute acids and reprecipitating with alkali. A colourless crystalline solid, m. p. 108° (decomp.). (Found: N, 5·6. $C_{27}H_{34}O_7N_2$ requires N, 5·60 per cent).

bis-*Cotarninoacetone methiodide*—On rubbing the acetone compound with a slight excess of methyl iodide a clear solution resulted and from this the crystalline methiodide separated almost immediately. Crystallisation from a large volume of hot water gave small yellow rod-shaped crystals melting at 210°. The crystals contained a molecule of water of crystallisation which was lost on drying at 110°/5 mm. over P_2O_5. [Found: H_2O (dried at 110°/5mm.), 3·77; I, 30·25. $C_{29}H_{38}O_7N_2I_2,2H_2O$ requires H_2O, 4·42; I, 31·11 per cent].

N-*methyl*-bis-*cotarnylideneacetone.*—A solution of the methiodide in hot water was treated with excess of 20% alkali. A yellow precipitate which soon changed into an oil separated, and the characteristic fishy odour of methylamine was also perceived. The mixture was boiled, cooled and the red oil extracted with chloroform. The semi-solid mass, left on evaporation of the chloroform, dissolved completely in cold dilute hydrochloric acid and the solution quickly deposited the *hydrochloride* as a mass of crystals which were recrystallised from a little hot water, m.p. 181-82° (decomp.). There was no loss of weight on drying the hydrochloride at 110°/5 mm. (Found: Cl, 13·0. $C_{29}H_{36}O_7N_2$, 2HCl, requires Cl, 12·22 per cent).

The *platinichloride* was also prepared and analysed. (Found: Pt, 19·51. $C_{29}H_{36}O_7N_2$, 2HCl, $PtCl_4$ requires Pt, 20·89 per cent).

N-*methyl*-bis-*cotarnylideneacetone methiodide.*—On stirring the oily base with methyl iodide, there was a vigorous reaction with considerable evolution of heat and the oil changed into a mass of bright yellow crystals. Recrystallisation from dilute alcohol furnished

small yellow needles, m.p. 168° (decomp.), not depressed by admixture with the product prepared directly from (I). The crystals dried at room temperature were found to contain water of crystallisation which was lost on drying at 78°/5 mm. over P_2O_5. [Found: H_2O, (dried at 78°/5 mm.), 3·88 ; I, 29·10. $C_{31}H_{42}O_7N_2I_2$, $2H_2O$ requires H_2O, 4·26; I, 30·08 per cent]. [Found (in material dried at 78° in vacuum): C, 46·9; H, 5·41. $C_{31}H_{42}O_7N_2I_2$ requires C, 46·05; H, 5·2 per cent].

bis-*Cotarnonideneacetone*.—The above mentioned methiodide was dissolved in hot water, excess of caustic soda added and the mixture distilled in steam. Trimethylamine was formed and was identified in the distillate by its picrate, m.p. 216°. On cooling, the yellow oil was extracted with ether and the dried ethereal solution evaporated. The cotarnonideneacetone was left as a yellow oil which solidified to a reddish mass on standing for two days. The product was proved to be free from nitrogen but could not be obtained in a sufficiently pure condition for analysis.

bis-*Cotarnylideneacetone*, identical with anhydrocotarninoacetone of Liebermann and Kropf (*loc. cit.*) (I). A suspension of finely powdered cotarnine (1 g.) in acetone (10 c.c.) was treated with 2 c.c. of 4*N*-sodium carbonate solution and the mixture shaken vigorously when the cotarnine gradually dissolved. After 6 hours the excess of acetone was removed on the water-bath and the residual oil left overnight when it solidified to a hard gritty mass. It was washed with cold water and dried on the porous plate. The crude product weighed more than 1 g. and melted at 74°-76°. Crystallisation from acetone gave colourless prisms, m.p. 83°.

Conversion of bis-*cotarnylideneacetone* (I) *into bis-cotarninoacetone* (II).—A solution of I (1 g.) in the minimum amount of rectified spirit was heated to 50° on the water-bath for 15 minutes and left overnight. On adding water the solution became milky and an oil separated which slowly hardened on rubbing. This was redissolved in alcohol, warmed and after 12 hours the solution diluted with water when the oil changed quickly into a mass of colourless crystals (0·9 g.) which, after drying in vacuum, melted at 150-51°, not depressed by admixture with (II).

Action of methyl iodide on (I).—The product (V), m.p. 168°, was identified with the methiodide obtained from (II) in two stages, and was decomposed by boiling alkali into *bis*-cotarnonideneacetone and trimethylamine.

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Influence of Temperature on the Carbon-Nitrogen Ratio of Soils.

By N. R. Dhar and S. K. Mukherji.

In a recent communication (Dhar, *J. Indian Chem. Soc.*, 1934, 11, 883) it has been stated that just as carbohydrates preserve the body proteins from undergoing oxidation, the carbonaceous matter present in the soil is likely to protect the soil protein from oxidation. This retarding influence of carbonaceous compounds on the oxidation of proteins to ammonia, and ammonium salts to nitrites and nitrates, appears to be a general phenomenon occurring in chemical, catalytic, physiological, soil and photochemical oxidation processes in which a mixture of organic substances is undergoing oxidation in air. The retarding influence of carbonaceous compounds on the velocity of the oxidation of proteins seems to control the corbon-nitrogen ratio.

Moreover, the ratio of carbon to nitrogen to be oxidised from a system would also depend on the ease with which these compounds, existing in mixtures, can undergo oxidation. It has been also stated in the previous paper that in starvation, the ratio of carbon to nitrogen oxidised in the metabolism of different animals is also fairly constant and is not far from 10.

It is generally believed that in fever when the body temperature is higher than the normal, the protein metabolism is relatively greater than in normal health, as will be evident from the following lines, "From a study of the excretion of nitrogen, together with a comparison of carbon dioxide and oxygen in the expired air, it has been thought, that the increased oxidation in fever affects specially the nitrogenous or protein constituents of the body" (MacCallum, "A Text Book of Pathology", 1925, p. 157). It is expected, therefore, that the nitrogenous compounds present in the soil of a warm place is likely to be oxidised at a relatively greater speed than those present in the soil of a cool place and hence the carbon-nitrogen ratio of the compounds existing in the soil will be higher in a warm than in a cold country.

In order to prove the validity of this view point, we have determined the carbon-nitrogen ratio of different soils collected from Bengal Behar, United Provinces and the Punjab. The carbon and nitrogen were estimated according to the method of Robinson, McLean and Williams. (*J. Agric. Sci.*, 1929, **19**, 315) by heating 5 g. of dry soil with strong sulphuric acid, anhydrous potassium sulphate and a few crystals of copper sulphate. The sulphur dioxide generated was absorbed in a standard solution of iodine. The nitrogen was determined by the liberation of ammonia on the addition of an excess of alkali to the solution obtained after oxidation by sulphuric acid. The following experimental results have been obtained.

TABLE I.

Bengal.

	Carbon.	Nitrogen.	Carbon/Nitrogen.
White rice fields (Nadia)	1·014%	0·112%	9·05
Red rice fields (Nadia)	0·849	0·096	8·84
Dacca soils			
Lab. No. 103 North Hazi Dacca Farm, unmanured under *Aman* paddy, surface soil	0·722	0·08	9·02
Lab. No. 104 Subhady, unmanured low *Aman* paddy land surface soil	1·372	0·146	9·39
Lab. No. 105 Bikrampur, uncropped, collected from the bank of a river, sub-soil	0·549	0·057	9·63
Lab. No. 106 Merida, unmanured *Boro* paddy very low land, surface soil	2·124	0 227	9·35
			Mean 9·14

TABLE II.

Behar (Pusa).

	Carbon.	Nitrogen.	Carbon/Nitrogen.
Permanent plot, complete manure collected in July 1932, analysed in April 1935	0·2913%	0·0313%	9·36
Do-Fresh soil collected in April 1935	0·3532	0·0406	8·7
Green manure, collected in July 1932, analysed in February, 1935	0·2331	0·025	9·32
Do-Fresh soil collected in April, 1935	0·2759	0·0332	8·31
No manure, collected in July 1932, analysed in February, 1935	0·2230	0·0238	9·37
Do-Fresh soil collected in April, 1935	0·2636	0·028	9·41
Green manure and super phosphate, collected in July 1932 analysed in April, 1935	0·248	0·0264	9·39
Do-Fresh soil collected and analysed in 1935	0·3509	0·0361	9·72
Farm yard manure collected in July 1932, analysed in April 1935	0·337	0·0313	10·8
Do-collected and analysed in April, 1935	0·3522	0·0361	9·75

Mean collected in July 1932 = 9·64.
Mean collected & analysed in April, 1935 = 9·17.

TABLE III.

United Provinces.

Allahabad.	Carbon.	(Uncultivated soils) Nitrogen.	Carbon/Nitrogen.
1	0·4464%	0·0434%	10·2
2	0·4854	0·04375	11·09
3	0·4352	0·0388	11·21
4	0·5481	0·0467	11·7
5	0·589	0·05	11·76
6	0·3075	0·026	11·82
7	0·5055	0·0458	11·03
8	0·504	0·0424	11·88
9	0·5356	0·0486	11·02
		Mean	11·3

TABLE IV.

Punjab soil.

	Carbon.	Nitrogen.	Cabon/Nitrogen.
Chkanwali Reclamation, collected and analysed in 1935.	0·5774%	0·04%	14·43
Ranjit-Kot (Shekhupura) collected and analysed in 1935	0·6442	0·04375	14·2
Hiyatpur (Behwal) collected and analysed in 1935	0·8464	0·0582	14·5
		Mean	14·37

The foregoing results show that the ratio of carbon to nitrogen is highest in the soil collected in the Punjab and the value is 14·37 and in the United Provinces it is 11·3. In Behar, it is 9·17 with freshly collected soils and 9·64 with soils collected in 1932 and analysed in 1935 and in Bengal, the ratio is 9·14,

The carbon-nitrogen ratio in soils of different countries seems to corroborate the above view point. The avarage ratio of 50 soils collected in England is 10. In Wales, the ratio is 9·2. In Washington state after long cultivation the ratio observed was 10·2. In Sudan the average is 12·6 and in Transval, it is 14·4 (compare Rusell " Soil Conditions andP lant Growth, " 1932, p. 314). From the foregoing results, it can be concluded that the nitrogenous compounds present in the soil of a warm place is oxidised more readily than those present in the soil of a temperate climate, just as in fever, the protein metabolism is greater than in normal health.

In publications from these laboratories, it has been emphasised that the chemical reactions taking place in the oxidation of the substances present in soils need not be always caused by micro-organisms as has been hitherto believed but may be photochemical and catalytic. These views regarding the soil processes have recently been supported by Corbet (*Soil Sci.*, 1934, **38**, 407), who has observed that the number of micro-organisms per grain of soil in the Malay Peninsula is only 500,000 as against 20 millions present in Rothamsted soils. He has made the following statements:—

"It has been submitted that, by permitting timber to decay on the cite of clearing, a considerable amount of readily available soil, nitrogen is locked-up as a consequence of the addition to the soil of material with a very high carbon-nitrogen ratio. If such locking-up of nitrogen in the body material of micro-organisms occurred it would be reflected in an increased soil microbial population, but the results presented in this paper show that such population increases do not take place.....

It seems evident that the fall in the nitrogen content of the soil to a lower level on subjection to higher temperatures must be ascribed to chemical and not to microbiological agency." The carbon-nitrogen ratio in ordinary soils appears not to be regulated by the energy requirements of the micro-organisms but is controlled by the ease with which proteins, amino acids and ammonium salts are oxidised by air catalytically or photochemically in presence of carbonaceous compounds. The energy-rich substances like carbohydrates, cellulose, etc., added to the soil may not increase the number of micro-organisms and cause a locking-up of nitrogen as body material but always decrease the velocity of the oxidation of the soil nitrogenous compounds and thus the ammonia production in soil decreases in presence of carbohydrates, cellulose, etc.

Summary.

1. Determinations of carbon-nitrogen ratio of soils collected in Bengal, Behar, United Provinces and the Punjab show that the value is highest in the Punjab and least in Bengal and Behar.

2. Results obtained in different countries show that this ratio in temperate climates is lower than that obtained in tropical climates.

3. Proteins present in the soil of a warm country are oxidised more readily than those present in a temperate climate, just as in fever the protein metabolism is relatively greater than in normal health. It appears that the oxidations taking place in the soil follow the same laws as those prevailing in animal metabolism, and the carbon-nitrogen ratio in soils is not an outcome of the microbial activity as has been hitherto believed.

Our best thanks are due to Rao Bahadur B. Viswanath, Dr. A. N. Puri, Prof. J. C. Ghosh, Dr. A. T. Sen, for supplying us samples of soils.

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Polymerisation of Some Unsaturated Fatty Acids.

By J. K. Chowdhury, A. C. Chakraborty and A. Majumder.

Polymerisation of simpler unsaturated acids such as acrylic acid, has been studied by Staudinger and others (*Helv. Chim. Acta*, 1929, **12**, 1107; *Ber.*, 1931, **64**, 2091; Pechmann and Rohm, *Ber.*, 1901, **34**, 427; Linnemann, *Annalen*, 1872, **163**, 369), who found that light has a powerful polymerising effect, while polymerisation of the methyl ester of crotonic acid has been studied by Pechmann (*Ber.*, 1900, **33**, 3323). Polymerisation of oleic acid and its methyl ester has been effected by Eichwald (*Z. angew. Chem*, 1922, **35**, 505) by means of silent electric discharge with the production of highly viscous products whose composition, however, remains unknown. The methyl ester of linolic acid had been polymerised by Kino (*Sci. papers of Inst. Phys. Chem Res. Tokyo*, 1933, **20**, 103) while ricinoleic acid has been polymerised by Grün (*J. Amer. Chem. Soc.*, 1909, **31**, 505) with the production of a solid rubber-like mass.

In the present investigation polymerisation of oleic and other unsaturated acids has been effected with the help of stannic chloride as a catalyst and highly viscous polymers have thus been obtained. These polymers, when decarboxylated, yielded lubricating oils similar to those obtained from petroleum.

Method of Polymerisation.

In a new Nessler's tube, provided with a mechanical stirrer, a definite quantity of oleic acid was taken and to this a known volume of stannic chloride was added, when considerable evolution of heat took place. The reaction was carried out at 100° in an oil-bath for 10 hours in an atmosphere of dry carbon dioxide. Evolution of hydrochloric acid gas was considerable in the beginning but towards the end it decreased. The product was then extracted with petroleum ether and washed thoroughly with water acidulated with hydrochloric acid until ash-free and was then washed free from all traces of the acid.

The ethereal solution was dried over anhydrous sodium sulphate and petroleum ether was then evaporated off completely under reduced pressure below 60°. To prevent back-rush it was found necessary to introduce a "T" piece connection between the evaporating apparatus and the suction, one end being connected to atmospheric air through a wash-bottle containing sulphuric acid.

Progress of polymerisation was observed by noting the changes of the physical constants.

TABLE I.

Progress of polymerisation with stannic chloride at 100°.

	Oleic acid.	Polymerised product with catalyst 5% by vol. (sample A.)	20% by vol. (sample B)
Sp. gr. at 28°	0·890	0·914	0·936
$n^{28°}$	1·448	1·452	1·462
Refractive const.	0·3006	0·2951	0·2936
$\eta_{28}°$	36·8El	153·1El	...
M. W. (cryoscopic)	280	553	1610
Iodine value (Hanus)	88·9	47·55	27·7
Acid value	198·6	150·3	124·1
Acid value (by heating with alcoholic potash)	...	151·4	124·8

Results in Table I show that the amount of stannic chloride added has a considerable influence on the degree of polymerisation of oleic acid. Its action is, therefore, not strictly catalytic. Evolution of heat during the polymerisation suggests the formation of intermediate compound of the unsaturated acid with stannic chloride. Stable compounds of stannic chloride with aromatic acids and with aliphatic dicarboxylic acids have been obtained by Hieber (*Annalen*, 1924, **439**, 97). The instability of these compounds activates the molecule and causes polymerisation. The decomposition of the intermediate compound with evolution of carbon dioxide indicates the carboxyl group being involved in the reaction with stannic chloride. Partial decarboxylation of the extremely stable fatty acids at a temperature not above 100° is rather significant. This decarboxylation

is further borne out by the fact that the polymer has a lower acid value than the theoretical.

Examination of Polymerised Product.

The product obtained by polymerisation of oleic acid was evidently a mixture of different polymer homologues, dissolved in one another.

Attempts were made to separate the various constituents by vacuum distillation. A solid or semisolid product distilled over at 210°-220°/6mm. and was found to be a mixture of stearic and oleic acids, while the residue was a highly viscous tarry product. In view of the large yield of stearic acid and its presence not being satisfactorily accounted for, the original oleic acid was subjected to a similar vacuum distillation but no solid stearic acid could be obtained. It was thus evident that stearic acid had been formed during the process of polymerisation of oleic acid. The quantity of the stearic acid (77·6%) in the mixture was calculated from iodine value of the distillate which consisted of oleic and stearic acids only. The experimental results are given below.

TABLE II.

Distillation of polymerised product.

	Polymerised oleic acid	Distillate at 210-20°.	Distillate at 220-25°.	Residue.
Iodine value (Hanus)	27·7	20·2	44·7	61·8
Acid value	124·1	124·1	145·5	130·2
M. W. (cryoscopic)	1610	306·5	...	750·3
Consistency	Semi-solid	Solid	Liquid	Tarry viscous
Yield	21·3 g.	5·6 g.	4·8 g.	7·3 g.

The physical and chemical properties of the residue indicate that considerable cracking had taken place and the molecular weight, acid value and other properties had been much affected by the heat to which it had been subjected during distillation.

The presence of stearic acid in the polymer might be attributed to the cracking of the polymer, resulting in the formation of new substances during distillation. The original polymerised product was, therefore, slightly cooled and then centrifuged and the solid, thus obtained, was found identical with stearic acid. The presence of stearic acid, therefore, could not be attributed to cracking, it must have been formed during polymerisation.

Molecular weight.—The rise in molecular weight of the polymerised product was determined by means of the cryoscopic method on the assumption that the Van't Hoff equation applied to dilute solutions of these high molecular substances. It will be seen from Table I that the highest average mol. wt. was 1610, obtained by treatment of oleic acid with 20% $SnCl_4$ (by volume) for a period of 10 hours. As this product is mixed with considerable amount of oleic and stearic acids, it is evident that the polymer is actually of a much higher order than that indicated by molecular weight determination.

Attempts were also made to determine the molecular weight from the specific viscosity on the assumption that the polymer was a long chain compound of the following type,

$$RCH{=}CHX + RCH{=}CHX = \begin{array}{cccc} CH & - & CH & - & CH & - & CH \\ | & & | & & | & & | \\ R & & X & & R & & X \end{array}$$

and hence the Staudinger formula $\eta_{sp}/C = K_m \cdot M$ was applicable. The K_m constant (29×10^{-4}) was determined with the help of the specific viscosity of pure oleic acid. The molecular weight of sample II (Table III) was found to be 448 (carbon tetrachloride) and 375 (benzene) by the Staudinger's method, while the mol. wt. by cryoscopic method was 1610. The Staudinger formula, which is applicable only to long fibre molecules, is not evidently applicable to this case.

Determination of physical properties.—The physical properties change in a regular manner with rise in molecular weight and hence with the degree of polymerisation. Changes in viscosity (η), refractive index (n), density (d) and iodine value may, therefore, be taken as indications of the degree of polymerisation. The relationship between molecular weight and physical and chemical constants will be evident from Table III.

TABLE III.

Relation between M. W. and physical and chemical constants.

Time of reaction = 10 hours.

No. of sample.	Catalyst used.	Temp. of reaction.	M.W.	$d^{28°}$	$n^{28°}$	Refractive constant.	$\eta_{25°}$	$\eta_{50°}$	Iodine value.	Acid value.
1	$ZnCl_2$	22-23°	...	...	1·4513	...	45·90° El	30·95°	63·14 Wj	196·88
2	,,	100	1029	0·9391	1·4560	0·2919	122·95	70·08	32·72	153·16
3	$AlCl_3$	26-27	610	0·9118	1·4524	0·2960	57·29	37·02	52·28	187·55
4	,,	100	...	...	1·4532	...	71·36	44·71	50·00	179·94
5	$SnCl_4$	26-27	...	...	1·4515	...	53·73	36·66	54·40	192·46
6	,,	100	1220	0·9481	1·4578	0·2897	285·11	142·85	19·48	138·35
7	$SbCl_3$	22-23	...	...	1·4506	...	41·36	28·76	65·30	199·98
8	,,	100	770	0·9189	1·4538	0·2946	72·83	45·59	46·00	177·63
9	$BiCl_3$	22-23	...	...	1·4502	...	35·87	25·31	67·32	200·31
10	,,	100	799	0·9216	1·4541	0·2939	113·43	65·76	37·62	169·02
11	$SnCl_4$	100	1610	...	...	...	...	...	27·7	124·1
Oleic acid	...	...	280	0·8871	1·4493	0·3027	34·63	24·44	80·00	201·76

Viscosity.—Relative viscosity has been determined by means of the Ostwald apparatus and is given in Engler units. It will be noticed that the viscosity rises with rise in molecular weight. In the region of lower molecular weights, the rise in viscosity is rather slow but in the case of larger molecules, a small increase in the molecular weight causes a considerable increase in the viscosity. This is evidently due to a few large molecules retarding the free flow of other molecules and thus causing abnormal increase in internal friction.

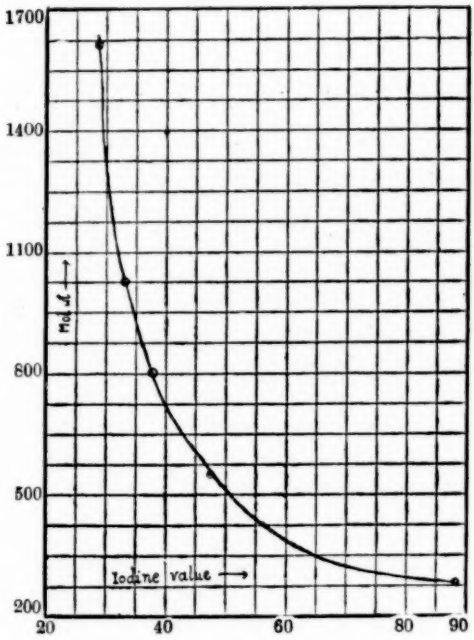
The rise in viscosity may be due to various causes, such as (*i*) size of molecules, (*ii*) solvation of the products, and (*iii*) association of comparatively small mols. as known in soap solutions. In the present instance, however, the latter two causes may be eliminated, as the molecular weight of the polymer remains unchanged in different solvents. Moreover, hydrocarbons obtained by decarboxylation of the polymer have also been found to consist of very large molecules and association of such homo-polar hydrocarbons is extremely unlikely. It may, therefore, be taken that the rise in viscosity correctly indicates the formation of high molecular polymers formed by the union of main valency and not by mere association. No quantitative expression relating viscosity to molecular weight could, however, be obtained.

Density.—Table III shows that density rises with polymerisation. This fact may be attributed to chemical union, for two or more molecules when combined by chemical valency would evidently require less space than the same number of monomer either free or associated in a loose manner.

Iodine value.—All the previous workers on polymerisation have taken the diminution in iodine value as proportional to increase in molecular weight. None of them have, however, taken into account the formation of saturated compounds (such as stearic acid in the present instance). The curve in Fig. 1 shows that with initial small rises in molecular weight, iodine value falls considerably but with subsequent large increase of the molecular weight slight diminution in iodine value takes place. This behaviour may be due to the very small initial concentration of stearic acid in the beginning having very slight influence on the iodine value but with the gradual accumulation of stearic acid iodine value data are affected considerably and in the region of high molecular weights the fall in iodine value is not thus proportional to the rise in molecular weight. A further reason why iodine value cannot be taken as a quantitative test for the progress of polymerisation

is that in this case the carboxyl group might be attached to the double bond or that decarboxylation during polymerisation may cause union to take place at other places than the double bond. Such decarboxylation has actually been observed to take place in this case indicating that union may take place at the centres occupied by carboxyl groups.

FIG. 1



Acid value.—Should the polymerisation take place at the double bond, the product should not change in acid value but it will be seen from Table I that the acid value progressively diminishes as polymerisation advances. This may be due to either of the following reasons:—

(*i*) Decarboxylation during polymerisation.

(*ii*) Weakness of the carboxyl groups in the polymerised product, the weakness increasing with the degree of polymerisation.

(*iii*) Linking of the carboxyl groups at the double bond to form intermolecular or intramolecular anhydrides.

The reasons for this reduction in acid value were carefully sought for. It was found that potentiometric titrations gave identical data as obtained by ordinary titrations. The anhydride formation may also be excluded, as the acid value did not change by heating the substance with alcoholic KOH and then titrating the excess of alkali. Evolution of carbon dioxide was, however, found to take place during polymerisation as has already been mentioned. This is evidently the reason for reduced acid value of the polymerised product as well as of the distillates obtained from the polymerised product.

Influence of Carboxyl Group on Polymerisation.

In order to see if the free carboxyl group has any effect on the course of polymerisation, the methyl ester of oleic acid was prepared and polymerised in the usual manner. It was found that changes in the different physical and chemical constants were very small indicating a rather slow progress in polymerisation. In this case protection of the carboxyl groups prevents decarboxylation and consequently polymerisation is here almost entirely caused by the double bond.

The same result was obtained from the glyceride, olive oil, which contained about 85% of unsaturated glycerides. Here also the polymersation was very much slower as in the case of the methyl ester. It is, therefore, evident that carboxyl group exercises a profound influence on the course of polymerisation.

TABLE IV.

Polymerisation of methyl ester of oleic acid.

Time = 10 hours. Temp. = room temp. and 100°.

	Original substance.	Product polymerised with catalyst 5% at 26°.	5% at 100°.	15% at 100°.
Sp. gr. at 28°.	0·871	0·877	0·894	0·897
$n^{28°}$	1·4410	1·4445	1·4485	1·4505
Refractive const.	0·3031	0·3031	0·2997	0·2997
Iodine value (Hanus)	81	81	61·7	58
$\eta_{28°}$	7·4 El	8·1 El	19 El	25·8 El

TABLE V.

Polymerisation of olive oil.

Time = 10 hours. Temp. = room temp. and 100°.

	Olive oil.	Product polymerised with catalyst 5% at 26°.	5% at 100°.	15% at 100°.
Sp. gr. at 28°.	0·913	0·923	0·925	0·946
$n^{28°}$	1·4600	1·462	1·4622	1·4635
Refractive const.	0·2993	0·2978	0·2975	0·2915
$v_{28°}$	68·9 El	97·2 El	107·4 El	125 El
Iodine value (Hanus)	82·8	76·2	75·7	62·8

Mechanism of Polymerisation.

An attempt to explain the mechanism of polymerisation should take into consideration (*a*) the formation of saturated stearic acid, (*b*) evolution of carbon dioxide, (*c*) lowering of the acid value, (*d*) the difference in the behaviour of the free acid and its ester, and (*e*) the large amount of stannic chloride necessary for satisfactory polymerisation. The polymerisation of oleic acid may evidently take place by

(*i*) Combination of a double bond with a double bond in any of the following manners:

$$RCH=CHX + RCH=CHX$$

$$-\underset{R}{CH}-\underset{X}{CH}-\underset{R}{CH}-\underset{X}{CH}- \quad \text{or} \quad \underset{R}{CH_2}-\underset{X}{CH}-\underset{R}{C}=CHX \quad \text{or}$$

(A) (B)

$$\begin{array}{l} RCH\text{——}CHX \\ \quad\;| \quad\;| \\ RCH\text{——}CHX \end{array}$$

(C)

(*ii*) Combination of carboxyl group with another carboxyl group to form acid anhydrides. (*iii*) Combination of carboxyl group with a double bond of the same molecule or of another molecule. (*iv*) Elimination of carboxyl group with evolution of carbon dioxide and hydrogen and combination at the active spot thus originated.

$$\begin{matrix} R-COOH \\ + \\ R-COOH \end{matrix} = \begin{matrix} R \\ | \\ R \end{matrix} + 2CO_2 + H_2$$

In the experimental results, no evidence of the formation of anhydrides could be obtained, nor could the formation of saturated tetracarbonic ring compounds (C) in the polymerised product or its distillates be traced. The reactions *i* (A), *i* (B) or reaction (*iv*) must, therefore, be responsible for the polymerisation of oleic acid. For reaction (*iv*), stannic chloride is necessary to form an intermediate compound similar to those formed with aromatic mono-carboxylic or aliphatic di-carboxylic acids (*loc. cit.*). Such intermediate compounds are decomposed with the evolution of carbon dioxide and hydrogen which reduces stannic to stannous chloride with evolution of hydrochloric acid and also reduces oleic to stearic acid. The stannous chloride formed is not in a position to unite with further molecules of oleic acid and hence a substantial quantity of stannic chloride has to be added to effect polymerisation. The evolution of carbon dioxide is responsible for the lowering of acid value. In the case of the methyl ester such evolution of carbon dioxide from the carboxyl group is prevented which explains the lower degree of polymerisation obtained in the case of the methyl ester and the glyceride of oleic acid.

Polymerisation of linolic acid.—Attempts were then made to polymerise linolic acid which contains a conjugated double bond in addition to the carboxyl group. In this instance the conjugated bond was found to be much more active and here carboxyl group played subsidiary part. The acid value, therefore, remained practically constant though the iodine value fell quickly and viscosity rose with the degree of polymerisation. Molecular weight determination of the final products showed that the degree of polymerisation was very high and several melecules combined to form the polymerised product, which was separated from stannic chloride by extraction with ether instead of petroleum ether.

TABLE VI.

Polymerisation of linolic acid.

Catalyst = stannic chloride. Time = 10 hours. Temp. = Room temp. and 100°.

	Linolic acid.	Linolic acid treated without catalyst	Product polymerised with catalyst 5% at 27°	15% at 100°.	20% at 100°.
Sp. gr. at 28°.	0·906	0·910	0·943	0·975	0·984
$n^{28°}$	1·4615	1·463	1·4815	1·4885	1·4915
Refractive const.	0·3030	0·3029	0·3021	0·2954	0·2944
$v_{50°}$	15·2 El	23·8 El	15·7 El	...	...
Acid value	207·8	207·9	205	202	209
Iodine value (Hanus)	182·5	155·2	108·6	50·2	45·6
M. W. (cryoscopic)	277	317	456	1544	1782

The possibilities of reactions are as follows:

$$RCH=CH-CH=CHX + RCH=CH-CH=CHX$$

$$\begin{array}{l} RCH-CH=CH-CHX \\ \quad\quad\quad\quad\quad\quad | \\ RCH-CH=CH-CHX \end{array} \quad \text{or} \quad \begin{array}{l} RCH-CH-CH=CHX \\ \quad | \quad\quad | \\ RCH-CH-CH=CHX \end{array}$$

(I) (II)

$$\begin{array}{l} \quad\quad\quad | \\ RCH-CH-CH=CHX \\ \quad | \\ RCH-CH-CH=CHX \\ \quad\quad | \end{array} \quad \text{or} \quad \begin{array}{l} \quad\quad\quad\quad | \\ RCH-CH-CH=CHX \\ \quad | \\ RCH-CH=CH-CHX \\ \quad\quad\quad\quad | \end{array}$$

(III) (IV)

In this case an eight membered as well as a four membered ring may be formed by the union of two molecules while an indefinite number of molecules may also combine together to form an open chain. As increasing molecular weight together with increase in viscosity is obtained, it would appear that bimolecular reaction must play only a minor part and that reaction (III) is mainly responsible for the formation of polymerised product.

Polymerisation of ricinoleic acid.—It would, therefore, be interesting to see how ricinoleic acid containing three reactive groups—one double bond, one hydroxyl group and one carboxyl group—behaves in the course of polymerisation. It will be found from the following table of experimental results that here the iodine value remains practically constant except when 20% or more stannic chloride are added. The polymerised product has the same acid value as the original product. The acetyl value, however, falls quickly. This would show that in this case double bond does not take part in the polymerisation but the hydroxyl group quickly disappears with the formation of an ether or ester type of compound. These esters are, however, very easily saponifiable and hence give the acid value of the original material. If ether formation were the only reaction, a bimolecular compound with a maximum molecular weight of 578 could be formed. But considerably higher molecular weight (*i. e.* 1836) has been found showing that at least six ricinoleic acid molecules are combined to form esters in the following manner:—

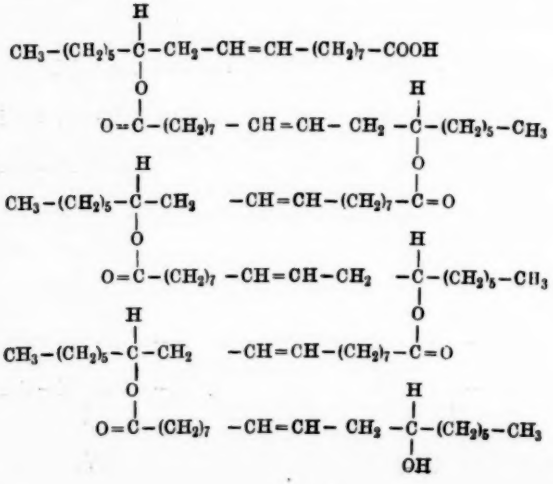


TABLE VII.

Polymerisation of ricinoleic acid.

Catalyst = stannic chloride. Time = 10 hrs. Temp. = Room temp. and 100°.

	Ricinoleic acid (original)	Polymerised product with catalyst			
		5% at 28°.	5% at 100°.	15% at 100°.	20% at 100°.
Sp. gr. at 28°.	0·9357	0·9376	0·9387	0·9625	...
$n^{28°}$	1·4625	1·463	1·465	1·482	1·492
Refractive const.	0·2940	0·2939	0·2947	0·2956	...
Iodine value (Hanus)	88·1	88·6	88·1	89·5	52
Acid value at room temp.	130	130	133	184	179
Acid value on heating	184·1	186·1	185·2	184·1	183·5
Acetyl value (Lewkowitsch method)	141	142	20	6	4·5
$\nu_{28°}$	201 El	215 El	379 El	...	...
M. W. (cryoscopic method)	...	...	...	675	1836

Decarboxylation of polymerised products.—The polymerised products, obained above, were decarboxylated with the production of highly viscous hydrocarbons similar to lubricating oils obtained from petroleum. This would seem to support the theory that petroleum hydrocarbons were formed from the polymerisation (and depolymerisation) of unsaturated fatty acids followed by decarboxylation. Such artificial lubricating oils are also interesting from an industrial point of view.

Decarboxylation was effected by heating the polymerised products (30 g.) at 365° with zinc dust (25 g.) for 2½ hours. The resulting product was acidified with hydrochloric acid and extracted with petroleum ether. The fall in acid value of the products indicated the degree of decarboxylation. The constitution of the hydrocarbons prepared under such drastic conditions could not, however, be

followed systematically. Similar products were obtained from the decarboxylation of the polymerised oleic, linolic, ricinoleic acids. These substances had high refractive index, were highly viscous and dark green in colour with a tinge of flourescence as in natural petroleum. The properties of the polymerised products and hydrocarbons obtained therefrom are given below. Owing to the high viscosity of the products, Ostwald tubes for determining viscosity could not be used.

TABLE VIII.

Polymerised	Colour.	Smell.	Refractive index.	Iodine value.	Acid value.
Oleic acid	Deep yellow	Rancid	1·462	27·7	124·1
Do decarboxylated	Dark green	Similar to lubricating oil	1·513	23·6	7·6
Linoleic acid	Deep yellow	Rancid	1·491	45·6	209
Do decarboxylated	Green	Like lubricating product	1·524	37·7	12·9
Ricinoleic acid	Deep yellow	Rancid	1·486	52·8	177·9
Do decarboxylated	Dark green	Like lubricating oil	1·516	44·6	11·1

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A Note on the Kaufmann's Thiocyanogen Value of Indian Butter Fat (Ghee).

By U. D. Budhalakoti and K. C. Mukherji.

Some interesting results were published by Paul Arup regarding the Kaufmann's thiocyanogen and iodine values of some samples of butter obtained from Irish dairies (*Analyst*, 1932, 57, 610). He observed that the linolic acid content of the butter fats, as determined by the application of the thiocyanogen and iodine values, was fairly constant (3·3–4·6%) and could be relied on for finding out the purity of a sample of butter fat. The present work may be taken as a continuation of the above work and its aim was to determine how far this holds true in the case of Indian butter fats which are likely to differ largely in their chemical composition. N. N. Godbole and Sad Gopal have already estimated the percentage of oleic and linoleic acids in different oils and fats (including butter-fat) by this method. (*Allgem. & Fett. Ztg.*, 1934, 435). The process may also perhaps be adopted as an additional method for finding out the purity of samples of butter fat.

Authenticated samples of butter or butter fat were obtained from the following places:—

Dayalbagh Dairy, Agra.	1. Cow butter.
	2. Buffalo butter.
Government Dairy, Bangalore.	1. Cow butter.
	2. Buffalo butter.
Cawnpore Agricultural College Dairy, Cawnpore.	1. Cow butter fat.
	2. Buffalo ,, ,,
Keventer's Dairy, Aligarh.	1. Cow butter fat.
	2. Buffalo ,, ,,
Etawah Ghee Suppliers.	1. Ghee No. 1.
	2. Ghee No. 2.

The samples of butter obtained as such were converted into fat by melting them in the air-oven at about 105° and decanting off the clear transparent fat and filtering. Before analysis all the samples of butter fat were dried in an air-oven at 105°−110° for about 3 hours and cooled.

Method of Analysis.

Iodine value.—Wij's method as given in Lewkowitsch was followed.

Thiocyanogen value (Kaufmann's).—The following procedure was adopted, as given by Wizoff (" Einheitliche-untersuchungs Methoden für oël und fett Industrie," 1930, II Auflage, p. 95).

400 C.c. of pure glacial acetic acid (Merck) were mixed with 40 c.c. of pure acetic anhydride and 120 c.c. of carbon tetrachloride (E. P.) and allowed to stand for a week. To half of the above solution 12·5 g. of pure lead sulphocyanide, prepared from lead acetate and potassium sulphocyanide and dried over phosphorus pentoxide for 15 days in the dark, were added and brought into suspension by shaking. To another half of the solution of glacial acetic acid and carbon tetrachloride, 3·2 c.c. of pure bromine (sp. gr. 3·188) was added. The bromine solution was then added to the suspended lead sulphocyanide little by little, each time shaking it vigorously till the colour of bromine was completely discharged. When all the bromine solution had thus been added and the bromine colour completely discharged, the solution was filtered through a previously dried filter paper. Precaution was taken at every step to exclude moisture. The clear colourless transparent solution, thus obtained, was used for the determination of thiocyanogen value in the same manner as is done in the case of Wij's iodine value.

0·2-0·3 G. of dried butter fat was taken in an iodine flask, 25-40 c.c. of thiocyanogen solution added, according to the quantity of fat taken. A blank was done exactly on similar lines. The reaction was allowed to proceed in the dark for 24 hours. An equal volume of 10% of KI solution was then added and the excess of thiocyanogen was titrated back with thiosulphate in terms of iodine liberated from potassium iodide.

The refractive indices were determined by the (Carl-Zeiss) Abbe refractometer. The various results obtained are tabulated below.

Serial No.	Description.		$n^{40°}$.	I_2 value.	SCN value.	Diff. between I_2 & SCN values.	Calc. linolic acid contents.	Remarks.
1.	Dayalbagh Dairy, Agra	Cow	1·4550	35·8	32·0	3·8	4·2%	
2.	Do	Buff	1·4550	37·6	34·4	3·2	3·5	Lowest linolic acid content.
3.	Government Dairy, Baugalore	Cow	1·4560	40·1	36·4	3·7	4·1	
4.	Do	Buff	1·4550	29·5	25·1	4·4	4·9	
5.	Agricultural College Dairy, Cawnpore	Cow	1·4570	49·9	45·0	4·9	5·4	Highest linolic acid content.
6.	Do	Buff	1·4560	40·4	36·8	3·6	4·0	
7.	Keventer's Dairy, Aligarh	Cow	1·4568	39·8	36·3	3·5	3·9	
8.	Do	Buff	1·4540	32·5	29·0	3·5	3·9	
9.	Etawah Ghee Suppliers	Ghee 1	1·4530	31·6	27·9	3·7	4·1	
10.	,,	Ghee 2	1·4520	18·0	18·0	0·0	0·0	

(*Note.* Sample No. 10 is obviously *no butter-fat* at all but is most probably hydrogenated oil or fat sold as *Vegetable Ghee* both because of the R. I., I. V. and SCN values.)

The percentage of linolic acid content in the above table was found by multiplying the difference between the iodine value and thiocyonogen value by 1·104, which factor depends upon the fact that the unsaturated acids contained in butter fat are essentially oleic and linolic acids, and in the case of oleic acid, the iodine and thiocyanogen value is the same, while in the case of linolic acid the thiocyanogen value is half of that of the iodine value.

Let S = % saturated acids,
O = % oleic acids, and
L = % linolic acids.

We can have three equations as follows :—

1. $S + O + L = 100$
2. $OS + 0·899\ O + 1·812\ L$ = Iodine value
3. $OS + 0·899\ O + 0·906\ L$ = Thiocyanogen value.

From 2 and 3, we have

$0·906\ L$ = Iodine value − thiocyanogen value.
or $L = 1·104$ (Iodine value—thiocyanogen value).

SUMMARY.

1. The range of iodine value of different samples of butter fat is very wide (30-50) (Literature gives this as 25-47. Holde-Bleyberg, 7th edition, p. 802). (Katalenwasser-stoff öle and Fette.)

2. The linolic acid content of authenticated samples of butter fat is fairly constant and the range of variation comparatively very low (3·5-5·4).

3. One of the samples (No. 10) was found to contain no linolic acid and hence it is easy to conclude that the sample did not contain any butter-fat at all.

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Putrefactive Decomposition of Bengal Silk Cocoon.

BY SIKHIBHUSHAN DUTT.

It is a well known fact that silk cocoon in presence of water undergoes decomposition very quickly and in the silk industry during the process of maceration of the cocoons in aqueous liquids for the removal of the yarn, very often a heavy odour of putrefaction is evolved, particularly if the temperature of the atmosphere is high. The products of such putrefaction have never been investigated by any one up to this time and although from the chemical point of view this would be quite interesting, yet the present investigation was undertaken from a slightly different standpoint. From a private communication from his friend Dr. V. N. Vyas of the King George's Medical College, Lucknow, the present author came to understand that the product of putrefaction of silk acted as a strong pressor substance for the heart, raising the blood pressure to a considerable extent. Apparently this must be due to the formation of some substances of great physiological activity during the process of putrefaction of silk cocoon and this was a sufficiently interesting field for research. Consequently the present investigation was undertaken with a view to elucidate the constitution of the compounds formed during the putrefaction.

A large supply of pierced silk cocoons was obtained through the courtesy of the Sericulture Department of the Government of Bengal, Berhampore. A preliminary examination of the cocoons revealed that they contained 25·6% of sericin, 70·4% of fibrin, 2·2% of moisture and about 2·0% of inorganic matter. The cocoons were coloured bright yellow and apparently contained a fairly large proportion of colouring matter in the form of carotin. Complete hydrolysis by hydrochloric acid and subsequent estimation of the amino acids by Fischer's ester method gave the following results, which can be compared with the result obtained by Abderhalden and Brahm (*Z. physikal. Chem.*, 1909, **61**, 256) by the hydrolysis of Bengal silk as given in the table below.

	From Bengal silk cocoon by the present author.	From Bengal silk by Abderhalden and Brahm.
Glycin	28·4%	30·5%
Alanin	22·85	20·0
Serine	5·75	1·8
Leucine	0·85	1·2
Aspartic acid	Traces	0·8
Glutamic acid	0·8	Traces
Phenylalanine	0·8	1·4
Proline	Traces	1·0
Tyrosine	12·8	10·0

From the above table it will be apparent that the really great difference between the two sets of results lies in the comparatively large proportion of serine obtained from the silk cocoon by the present author.

The cocoons on maceration with about 50 times their weight of water and incubation at 37° about a week, underwent extensive putrefaction and lost 35% of their weight during the process. The liquid expressed from the undecomposed fibres had a most nauceating odour, and on systematic working up as described in the experimental portion of the paper, yielded the following substances in the pure state in the form of their hydrochlorides: ammonia, methylamine, ethylamine, *p*-hydroxyphenylethylamine and aminoethanol (4·3%, 1·8%

5·8%, 2·1% and 0·3% respectively). Carbon dioxide was freely evolved during the process of putrefaction. From the afore-mentioned results it is quite apparent that the process of putrefaction of silk cocoon involved mainly two stages, namely, one of hydrolysis of the protein matter into amino acids and the other of elimination of carbon dioxide from the amino acids with the formation of amines, the two processes following each other so closely that at no time any great concentration of amino acids can be detected in the putrefying material. The amines mentioned above being well known pressor substances, particularly *p*-hydroxyphenylethylamine or tyramine, there is little wonder now that a decoction of putrefied silk cocoon would act as a strong pressor substance for the heart. The fibrous matter left after the putrefaction was over was found to undergo very little change on further treatment in the same way, and was practically pure fibrin. It had almost the lustre as ordinary silk fibre but only about half the strength. It was practically completely bleached after the putrefaction. It was not further examined chemically. It was also interesting to note here that the large proportion of ammonia evolved during the putrefaction must be due to the further degradation of the amines.

Experimental

100 G. of silk cocoons were macerated with 5 litres of distilled water and the mixture, contained in an wide mouth extraction flask, was incubated at 37° for 7 days. At the end of that period the light brown cloudy liquid with a disgusting odour of putrefaction was squeezed off from the fibrous material and filtered first through cloth and then through filter paper. The filtrate which had a strongly alkaline reaction was neutralised with dilute hydrochloric acid and evaporated to dryness at first over free flame and finally on the water-bath. A dark brown slightly sticky, crystalline solid (yield 19·8%) was left behind and from a large number of experiments of the above type a total quantity of 268 g. of the solid was collected. This was refluxed with 3 litres of absolute alcohol and 30 g. of animal charcoal for nearly 12 hours and then filtered. The filtrate on cooling deposited a large amount of colourless crystalline needles which were filtered off, washed with absolute alcohol and dry ether and recrystallised from absolute alcohol. This product was termed *fraction* A.

The residue on the filter paper was extracted with boiling water, and the filtered extract evaporated to a small volume and allowed to

stand when a large amount of colourless feathery crystals separated out. These were filtered off and recrystallised from a small quantity of boiling water. This was termed *fraction* B.

The mother liquor from fraction A was evaporated to about 500 c.c. and allowed to stand in the refrigerator for 24 hours, when another crop of colourless needle shaped crystals separated out. They were filtered off and recrystallised from pure methyl alcohol in colourless hygroscopic needles. This portion was termed *fraction* C.

The mother liquor from the above was treated with dry petroleum ether until an oily precipitate was no longer formed. On allowing to stand in the refrigerator the oily product solidified and was filtered off and washed with dry petroleum ether. It was recrystallised from a mixture of equal volumes of dry petroleum ether and absolute alcohol in colourless prismatic needles. This was termed *fraction* D.

The mother liquor and the washings from the above were collected together and the whole evaporated to dryness. A pale brownish white, highly hygroscopic crystalline solid was left behind which was washed with small quantities of petroleum ether and finally recrystallised from a mixture of equal proportions of chloroform and benzene. The substance was thus obtained in pale cream coloured highly hygroscopic needles. This was termed *fraction* E.

Examination of the various Fractions.

Fraction A.—This melted at 269° and was easily soluble in water. On treatment of the aqueous solution with dilute caustic soda or ammonia an immediate white precipitate was formed which was filtered off and crystallised from xylene in colourless leaflets melting at 161° and identified to be *p*-hydroxyphenylethylamine or tyramine. The m. p. was unaltered on admixture with a genuine sample of tyramine obtained from Messrs. E. Merck. (Found: N, 10·61. Calc. for $C_8H_{11}ON$: N, 10·2 per cent).

Fraction B.—This did not melt at all but gradually sublimed on heating without leaving any residue. On treatment with caustic soda a strong smell of ammonia was evolved. The substance was identified as ammonium chloride.

Fraction C.—This melted at 223-24° and crystallised in two forms, needles and leaflets. On treatment with dilute caustic soda no precipitate was formed, but a strong ammoniacal fishy odour was evolved. Aqueous solution of the substance gave an immediate preci-

pitate with aqueous picric acid which on recrystallisation from dilute alcohol melted at 206°. The substance was identified to be methylamine hydrochloride and the m. p. was not depressed on admixture with a sample of the genuine substance obtained from Messers E. Merck. (Found: N, 20·9. Calc. for CH_3NH_2, HCl: N, 20·7 per cent).

Fraction D.—This melted at 73°-78° and crystallised both in the form of prismatic needles and glistening leaflets. It was easily soluble in water and on treatment of the aqueous solution with dilute caustic soda no precipitate was formed, but a strong fishy odour was evolved. The aqueous solution gave immediate precipitates with dilute solutions of mercuric chloride, platinic chloride and chromic acid but not with aqueous picric acid. The crystalline substance on treatment with acetic anhydride and sodium acetate gave a crystalline acetyl derivative, m. p. 204°. The substance was identified to be ethylamine hydrochloride and was in all respects identical with a genuine sample of the substance prepared from Merck's 93% alcoholic ethylamine solution. The melting point was also not depressed on admixture with the prepared sample. (Found: N, 17·6. Calc. for $C_2H_5N\,H_2$, HCl: N, 17·1 per cent).

Fraction E.—This melted at 96°-97° and was extremely hygroscopic. The aqueous solution was slightly acidic in reaction and gave immediate precipitates with aoueous platinic chloride and picric acid. The picrate crystallised from alcohol in large lemon-yellow hexagonal tablets melting at 158-59°. The substance was identified to be the hydrochloride of aminoethanol and on account of the highly hygroscopic character of the hydrochloride, the picrate was analysed. [Found: N, 19·0. $C_2H_7NO,C_6H_3(NO_2)_3O$ requires N, 19·3 per cent].

The author wishes to express his best thanks to the Deputy Director of Sericulture, Government of Bengal, Berhampore, for a generous supply of pierced silk cocoons.

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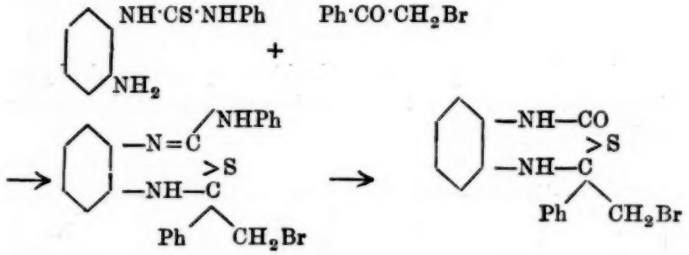
A Note on the Condensation of ω-Bromoacetophenone with 1-*o*-Aminophenyl-3-Phenylthiocarbamide.

By Kumud Behari Pathak.

In the course of an investigation on the action of ω-bromoacetophenone upon 1-*o*-aminophenyl-3-arylthiocarbamides, Ghosh (*J. Indian Chem. Soc.*, 1931, **8**, 71) obtained certain well-defined condensation products which he formulated as (II). The course of the reaction was represented as follows:



(I) (II)

The author considered such reactions as highly improbable. Because it has been shown by a large number of investigators that the bromine atom of ω-bromoacetophenone is *always* eliminated as hydrogen bromide in its condensation with a compound with the grouping NH·CS·NHR the final product being the hydrobromide of a cyclic base, having sulphur in the ring. In the case of 1-*o*-aminophenyl-3-arylthiocarbamides Ghosh assumed a greater reactivity of the ketonic group without adducing any experimental evidence thereof. It was, therefore, thought necessary to repeat Ghosh's experiment and ascertain the real nature of the compound to which he assigned the constitution (II). In dilute acetic acid solution the condensation product was an uncrystallisable oil. In 95% acetic acid solution a crystalline product was obtained in a very poor yield which on being thrice crystallised from glacial acetic acid melted at 223° (decomp.). (Found: C, 51·1; H, 4·09; Br, 24·0. Calc. for $C_{15}H_{13}ON_2SBr$: C, 51·0; H, 3·72; Br, 22·8 per cent). Ghosh's compound melted at 230°

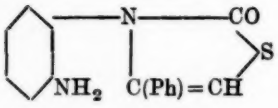
(decomp.). The properties and analysis, however, agreed with those of Ghosh and the two compounds are regarded as identical. That this compound is the hydrobromide of a weak base is demonstrated by the following facts:

(*i*) An aqueous-acetone solution of the substance was acidic to Congo-red paper.

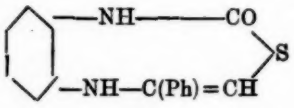
(*ii*) The substance liberated carbon dioxide when triturated with cold sodium bicarbonate solution and was converted into a base, m. p. 164°, which crystallised from alcohol in long pointed light straw-yellow needles. (Found: N, 10·44; $C_{15}H_{12}ON_2S$ requires N, 10·41 per cent).

(*iii*) The same hydrobromide was obtained when the reaction was allowed to proceed in alcoholic solution and the base, liberated by pyridine, melted at 164°.

These facts definitely prove that Ghosh's compound is the hydrobromide of a base melting at 164°, which may be given the constitution (III) or (IV).



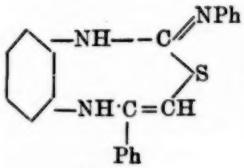
(III)



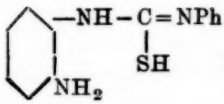
(IV)

The reaction involves the elimination of aniline during the condensation and surprise was expressed by Ghosh that a compound of the type (I) should so easily eliminate aniline. In fact instances of such type of hydrolysis where the aniline group is attached to the ring by means of a single bond are hardly to be met with. If, on the other hand, the intermediate componnd is supposed to have the structure (V), there is no difficulty whatsoever of an explanation, since the easy hydrolysability of the :C=NR group is well known. Ghosh also made another interesting observation that when 1-*o*-aminophenyl-3-allylthiocarbamide is condensed with ω-bromoacetophenone the allyl group, unlike the phenyl group, is not eliminated as allylamine. This appears to be due to the different character of the phenyl and allyl group. In the former case the intermediate compound reacts as (VI) whereas in the latter case as (VII), the phenyl group having a definite negative character. In the condensation product, therefore,

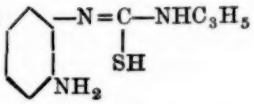
the allylamino-group is attached to the ring by means of a single bond and hence no hydrolysis.



(V)



(VI)



(VII)

In conclusion I wish to express my thanks to Dr. P. K. Bose for his advice during the course of the investigation.

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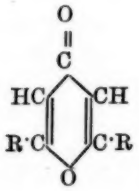
Reactivity of Carbonyl Group in γ-Pyrones and in γ-Pyridones.

BY D. N. BEDEKAR, R. P. KAUSHAL AND S. S. DESHAPANDE.

The structure of γ-pyrones (I) and that of γ-pyridones (II) are not in agreement with the fact that in general these compounds do not form an oxime or a phenylhydrazone.

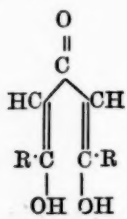


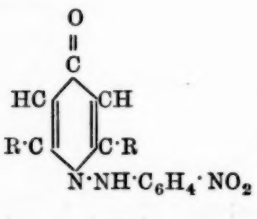
(I)

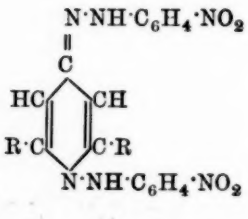
(II)

We, however, find that by using the more reactive *p*-nitrophenylhydrazine in place of phenylhydrazine, chelidonic ester (I, R = CO_2Et) gives its nitrophenylhydrazone which on hydrolysis gives back chelidonic ester. This reaction of a true ketone justifies the structure (I) for this pyrone. 3:5-Dibromochelidonic ester similarly gives its nitrophenylhydrazone.

When xanthochelidonic ester (acetone dioxalic ester III, R = CO_2Et) is, however, treated with the same reagent two products are obtained of the composition $C_{17}H_{17}O_7N_3$ (m. p. 146°) and $C_{23}H_{22}O_8N_6$ (m.p. 210°). The former is isomeric with the nitrophenylhydrazone of chelidonic ester and is regarded as (IV) formed by the action of nitrophenylhydrazine on the dienolic form (III) of acetone dioxalic ester. The compound (m.p. 210°), which can also be prepared by the interaction of nitrophenylhydrazine and (IV) is obviously its nitrophenylhydrazone (V).


(III)


(IV)


(V)

This reaction was extended to other triketones of the type of acetone dioxalic ester. Thus diacetylacetone and nitrophenylhydrazine are found to react in molecular proportion to give a product of the composition $C_{13}H_{13}O_3N_3$. This could not be the nitrophenylhydrazone of dimethyl pyrone, as dimethylpyrone itself does not form a nitrophenylhydrazone. The compound must, therefore, be a pyridone, formed as in the case of acetone dioxalic ester. Moreover, as it forms a nitrophenylhydrazone $C_{19}H_{18}O_4N_6$ the pyridone must be a true ketone. The structures of diacetylacetone, of the pyridone and of its nitrophenylhydrazone are (III), (IV) and (V) (R = Me).

Somewhat similar results have been obtained from dipropionylacetone by Deshapande, Dingankar and Kokil (*J. Indian Chem. Soc.*, 1934, **11**, 595).

Although nitrophenylhydrazine has no action on dimethyl-, diethyl-, or dipropylpyrone, it reacts energetically upon pyrone itself

(I, R=H) giving a product $C_{17}H_{14}O_4N_6$, in the formation of which two molecules of the reagent have reacted. By decreasing the proportion of the reagent no other product could be isolated. As the two oxygen atoms in the pyrone are the only points of attack by the reagent the compound must have the structure V (R=H). It is a base and forms a chloroplatinate. On dry distillation with caustic potash a few drops of a strongly basic liquid soluble in water and having odour of pyridine were obtained, but the quantity was too small for further investigation.

Chelidonic acid (I, R=CO_2H) and comanic ester (I, R=H; R=CO_2Et) similarly react with two molecules of nitrophenylhydrazine yielding corresponding products of structure (V). In no case could any definite product of the reaction of one molecule of nitrophenylhydrazine be isolated.

The nitrophenylhydrazones of *N*-substituted pyridones (V) must have been formed from the corresponding pyrones (I) *via* either (*a*) the *N*-substituted pyridones (IV), or (*b*) the nitrophenylhydrazones of the pyrones. The latter route seems to be unlikely because nitrophenylhydrazone of chelidonic ester does not react with nitrophenylhydrazine. In the former route attempts to get the *N*-substituted pyridones (IV) have been unsuccessful. This is probably due to the fact that the rate of phenylhydrazone formation of such *N*-substituted pyridones as have been actually isolated (IV, R=CO_2Et or Me) is quite rapid (less than 10 minutes for completion of the reaction), as compared to the rate of their own formation. Indeed in the formation of (IV) from (III) using 1 molecule of nitrophenylhydrazine some quantity of (V) is invariably produced although the reaction is allowed to go only for a short time.

Experimental.

Nitrophenylhydrazone of chelidonic ester.—The pyrone and the reagent in molecular proportions were heated together in absolute alcoholic solution for half an hour. On removing excess of the solvent and rubbing, the phenylhydrazone separated as a reddish yellow mass. It crystallises from alcohol in golden yellow needles and from benzene in scarlet needles, m. p. 216°. (Found: C, 54·0; H, 4·2; N, 11·8. $C_{17}H_{17}O_7N_3$ requires C, 54·4; H, 4·5; N, 11·2 per cent).

Hydrolysis of the phenylhydrazone.—The compound was refluxed in glacial acetic acid solution in a current of dry hydrochloric acid

for 1 hour. On cooling and pouring in water the unchanged phenylhydrazone precipitated which was filtered off. On making the filtrate feebly alkaline, an oil separated which gradually solidified and on crystallisation from petroleum melted at 63° and was identified as chelidonic ester by mixed melting point.

The nitrophenylhydrazone of dibromochelidonic ester, which was prepared as above, crystallises from alcohol in needles, m. p. 120°. (Found: Br, 30·9. $C_{17}H_{15}O_7N_2Br_2$ requires Br, 30·0 per cent).

Action of nitrophenylhydrazine on acetonedioxalic ester.—When equimolecular proportions of the two substances react for a short time in boiling absolute alcohol the pyridone (IV, R=CO_2Et) is the main product formed together with some amount of its nitrophenylhydrazone (V, R=CO_2Et). The longer the duration of heating, the greater becomes the yield of (V) and in one hour the whole reaction product consists practically of (V). The products are separated by means of alcohol in which (V) is less soluble than (IV). If the reaction is carried out in glacial acetic acid, the pyridone (IV) is more conveniently obtained. The pyridone crystallises from alcohol and melts at 146°. (Found: C, 54·2; H, 4·8; N, 10·9. $C_{17}H_{17}O_7N_3$ requires C, 54·4; H, 4·5; N, 11·2 per cent).

The nitrophenylhydrazone of the pyridone crystallised from acetic acid and melted at 210°. (Found: C, 53·6; H, 4·5; N, 16·7. $C_{23}H_{22}O_8N_6$ requires C, 54·1; H, 4·3; N, 16·4 per cent).

Action of nitrophenylhydrazine an diacetylacetone.—On refluxing in absolute alcohol for 10 minutes molecular proportions of diacetylacetone and nitrophenylhydrazine, the pyridone (IV, R=Me) separated on cooling as a pale yellow solid. It crystallised from alcohol in starshaped clusters, m, p. 136°. (Found: C, 60·3; H, 5·3; N, 15·8. $C_{13}H_{13}O_3N_3$ requires C, 60·0; H, 4·8; N, 16·2 per cent).

The nitrophenylhydrazone of the above pyridone (V, R=Me) was obtained from the pyridone in glacial acetic acid. It was, however, more conveniently prepared by heating for 10 minutes on a water-bath diacetylacetone (1 mol.) and nitrophenylhydrazine (2 mols.) dissolved in glacial acetic acid. Crystallised from acetic acid it melts at 215°. (Found: C, 58·1; H, 4·3; N, 20·8. $C_{19}H_{18}O_4N_6$ requires C, 57 8; H, 4·6; N, 21·3 per cent).

Action of nitrophenylhydrazine on pyrone.—When pyrone (1 mol.) and nitrophenylhydrazine (2 mols.) were warmed on a water-bath in glacial acetic acid for 5 minutes the nitrophenylhydrazone of pyridone (V, R=H) was formed as a yellow solid. After crystallising from

pyridine it melts at 242°. (Found: C, 55·7; H, 4·1; N, 22·6. $C_{17}H_{14}O_4N_6$ requires C, 55·7; H, 3·6; N, 22·9 per cent).

Action of nitrophenylhydrazine on chelidonic acid.—This was carried out as in the case of pyrone, but dilute acetic acid was used owing to chelidonic acid being sparingly soluble in glacial acetic acid. The nitrophenylhydrazone of pyridone (V, R=CO_2H) crystallised frm methyl alcohol as yellow needles, m. p. 210°. (Found: C, 49·8; H, 3·3; N, 18 4. $C_{19}H_{14}O_8N_6$ requires C, 50·0; H, 3·1; N, 18 5 per cent).

Action of nitrophenylhydrazine on comanic ester.—This was carried out as in the last two cases substituting alcohol in place of acetic acid. The nitrophenylhydrazone of pyridone (V, R=H; R=CO_2Et) crystallised from acetic acid in yellow prisms, m. p. 220°. (Found: C, 54·8; H, 4·0; N, 19·4. $C_{20}H_{18}O_6N_6$ requires C, 54·8; H, 4·1; N, 19·2 per cent).

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The Chemistry of Jute-lignin. Part VII. Behaviour of Organic Compounds towards ClO_2 and its Significance on the Constitution of Lignin.

By Pulin Behari Sarkar.

Schmidt and co-workers (*Ber.*, 1922, **55**, 1529) have tried the action of ClO_2 on a number of organic compounds and have found that water-soluble products, mainly aliphatic acids and in many cases chloro-compounds are obtained when a free phenolic group is present. The well known action of ClO_2 on lignin which yielded oxalic acid, carbon dioxide and maleic acid but no aromatic compound, was interpreted as an evidence in favour of the presence of a free phenolic group in lignin. This view was also corroborated by Fuchs and Honsig (*Ber.*, 1926, **59**, 2850).

The action of diazomethane in introducing one methoxyl group (assuming a molecular weight of 820) in lignin as observed by Freudenberg ond Hess (*Annalen*, 1926, **448**, 124) as well as by Fuchs and Horn (*Ber.*, 1929, **62**, 1691), was also used as an argument in support of the free phenolic group theory. The facts that cellulose and other polysaccharides behave similarly with diazomethane and that Willstätter-lignin is insoluble in dilute alkalis, compelled Freudenberg to change his views, so that he made no provision for any such phenolic group in his constitutional formula for lignin ("Tannin, Cellulose und Lignin", 1933, 123.)

In view of these facts, it was thought worth while to study the action of ClO_2 on more varied types of organic compounds in order to see if the conclusions drawn from the reactions of Schmidt and others were really justified. As will be seen in Table I, all aromatic bodies with a free phenolic group are very readily attacked ; but it has also been found that when these phenolic groups are protected either by methylation or acetylation, the resulting compounds are still susceptible to oxidation by ClO_2 though less readily (Table II). Further aliphatic OH group in the side-chain attached to the benzene ring (*e.g.* benzyl alcohol) is also oxidised by ClO_2 (Table III) but when it is occupied by methoxyl or acetyl group, it is no longer acted upon by ClO_2. As lignin contains beyond doubt, more than one methoxyl

group attached to the benzene ring, and hydroxyl group attached to the side-chain, it is obvious that the fact that it is acted upon slowly by ClO_2, cannot in any way prove the existence of any aromatic hydroxyl group in the molecule. The comparative resistance of acetylated or methylated lignin to the action of ClO_2, may thus be due to the protection of hydroxyl groups in the side-chain.

Subsitituents like Cl, Br and NO_2 make the phenols comparatively more resistant to the action of ClO_2 and as chloro-, bromo-, and nitrolignins as well behave in a similar way, it may be inferred that these substituents enter at least partly the benzene ring, when lignin is chlorinated, brominated or nitrated.

It has been observed that the dioxymethylene group in lignin is quite resistant towards ClO_2. It is, therefore, unlikely that ClO_2 opens up free phenolic group by the removal of the dioxymethylene group from lignin and thus exposing free phenolic groups to be acted upon.

It has been found that when aliphatic hydroxyl groups are methylated or acetylated, they resist the action of ClO_2. It has also been found that methoxyl or acetyl value of jute, delignified by the ClO_2 method, is due to pectin matter. As these groups in delignified fibre are not acted upon by ClO_2 it may be concluded that pectin is entirely aliphatic in nature, thus corroborating the views of Ehrlich and Sommerfield (*Bio chem. Z.*, 1925, **168**, 263). As pectin obtained from jute is perfectly resistant to ClO_2, it is evidently dissimilar from lignin in structure and hence the author is opposed to the view that lignin owes its origin to pectin.

It has further been observed that small amounts of chlorolignin are invariably formed when ClO_2 acts on lignin. The amount of chlorolignin formed by the action of ClO_2 gas is considerably less than that formed by ClO_2 solution. This is probably the reason why sodium sulphite or acetic acid, both excellent solvents for chlorolignin, had to be used in Schmidt's process of delignification, while thorough washing with water is generally sufficient if ClO_2 in gaseous form is used for the purpose. This chlorolignin is evidently responsible for the slight yellow colour of the delignified fibre. As the chlorolignin resists the action of ClO_2 and of 42% HCl, it has often been mistaken for lignin. The chloro-lignin has actually been isolated and analysed as regards its solubility, chlorine-content, methoxyl etc. and found to be almost identical with that obtained in the usual way with chlorine.

Incidentally it may be remarked that HCl-lignin, obtained from teak-wood (by 42% HCl), takes a much longer time to dissolve when gaseous ClO_2 is passed through its aqueous suspension and leaves behind more residue of chloro-lignin than lignin from jute; this fact supports the view of the author (*J. Indian Chem. Soc.*, 1933, **10**, 263) that jute-lignin is less highly polymerised than wood-lignins.

Experimental.

ClO_2 was prepared by warming on the water-bath (35°-40°) an intimate mixture of chemically pure oxalic acid (20 g.) and potassium chlorate (25 g.) with 80 c.c. of dilute sulphuric acid (100 c.c. of sulphuric acid diluted to 325 c.c.) in a round bottomed flask fitted with all glass connections and absorbing the gas in a series of gas-washers containing water. These were collected and made to a litre and 5 c.c. of it were diluted with 20 c.c. of water and titrated with $N/10$-thiosulphate after adding 3 c.c. of $2N$-potassium iodide solution, and 10 c.c. of N-sulphuric acid in the usual way. The original solution was diluted with water so as to be approximately $0{\cdot}25N$. The solution was preserved in a bottle wrapped with black paper and fitted with a well ground stopper. The strength remains practically unchanged when kept in a cool place provided the stopper is made gas-tight with vaseline.

About 0·5 g. of the substance (pulverised if solid) was taken in an Erlenmeyer flask with a good stopper, 10 c.c. of the ClO_2 solution were added and the stopper closed immediately. It was kept in a dark cool place and shaken mildly from time to time. After several hours (12-48) the solution was titrated with thiosulphate as described above, after adding 20 c.c. of cold water. Duplicate experiments were always done and the mean value for thiosulphate was accepted. The strength of ClO_2 was determined every time before exposure and also after the same period in a blank experiment in a similar flask, the mean being taken as the original titre. The difference was always found to be quite negligible (0·1—0·2 c.c.) and so the complicated arrangement of Schmidt and Graumann (*Ber.*, 1922, **54**, 1862) was not adopted. More concordant results were obtained if the flask was cooled to 5°-10° before the addition of potassium iodide and titration. The experimental results are given in Table I, II and III below.

TABLE I.

Room temp. = 22°—25°

Substance.	Time.	Original titre (thio.)	Final titre. (thio.)	Substance.	Time.	Original titre (thio.)	Final titre.
Phenol	12 hrs.	21·50 c.c.	3·10 c.c.	*p*-Hydroxybenzoic acid	46 hrs.	21·20 c.c.	2·20 c.c.
Resorcinol	,,	,,	0·0	Guiacol	,,	,,	1·10
Catechol	,,	,,	,,	Eugenol	,,	,,	0·50
Hydroquinone	,,	,,	30·1	*iso*Eugenol	,,	,,	1·0
m-Cresol	24	21·35	1·80	*cyclo*Hexanol	,,	21·00	1·80
p-Cresol	,,	,,	0·15	Orcinol	40	,,	0·10
Salicylic acid	,,	,,	0·50	Protocatechuic acid	,,	,,	0·30
Vanillin	,,	,,	2·15	Pyrogallol	,,	,,	0 0
Vanillic acid	,,	,,	4·30	Phloroglucinol	48	20·90	0·0
m-Hydroxybenzoic acid	48	21·20	0·20	Gallic acid	,,	,,	0·05

By taking equimolecular proportions of the phenolic compounds and exposing them to the action of ClO_2 for the same time and at the same temperature, it has been found that the greater the number of the free hydroxyl groups, the more readily it is decomposed. The results are not shown here as it has no direct bearing on the constitution of lignin.

TABLE II.

Room temp. = 21—23°.

Compound.	Time.	Original titre (thio.)	Final titre (thio.)	Compound.	Time.	Original titre (thio.)	Final titre in (thio.)
Anisol	24 hrs.	20·35 c.c.	10 20 c.c.	Acetyl salicylic acid	36 hrs.	20·0 c.c.	13·7 c.c
Phenetol	,,	,,	15·45	Vanillic acid dimethyl ether	,,	,,	10·50
Phenyl acetate	36	,,	12·75	*m*-Methoxybenzoic acid	40	,,	7·65
Resorcinol dimethyl ether	48	20·25	6·90	*p*-Methoxybenzoic acid	,,	,,	7·80
Catechol dimethyl ether	,,	20·20	8·70	*cyclo*Hexanol methyl ether	45	19·50	12·0
Hydroquinone dimethyl ether	,,	,,	7·70	Phloroglucinol trimethyl ether	,,	,,	9·75
m-Cresol methyl ether	46	,,	9·50	Pyrogallol trimethyl ether	,,	,,	8·70
p-Cresol methyl ether	,,	,,	8·90	Benzoquinone	32	,,	40·0
Salicylic acid methyl ether	,,	,,	8·85	Acetophenone	,,	,,	19·00

TABLE III.

Room temp. = 20—24°.

Substance.	Time.	Original titre (thio).	Final titre (thio).	Substance.	Time.	Original titre (thio).	Final titre (thio).
Benzene	48 hrs.	21·50 c.c.	21·25 c.c.	*m*-Chlorophenol	24 hrs.	19·90 c.c	9·0 c.c.
*cyclo*Hexane	,,	,,	21·30	Phthalic acid	48	21·50	21·30
Toluene	,,	,,	10·80	Cinnamic acid	,,	21·0	19·90
p-Xylene	,,	,,	8·0	Furfural	,,	,,	nil
o-Xylene	,,	,,	7·0	Pyromucic acid	,,	,,	nil
Benzoic acid	,,	,,	21·25	Methylated lignin (34·41% OMe)	,,	19·90	8·90
Benzaldehyde	,,	,,	0·30				
Mandelic acid	45	20·90	14·90	Acetylated lignin (33·32% acetic acid)	48	,,	11·0
Benzyl alcohol	,,	,,	Nil				
Piperonal	48	,,	9·80	Pectin from jute	36	19·5	18·90
Piperonylic acid	,,	,,	20·80	Cellulose triacetate	36	19·50	19·10
Safrol	,,	20·50	·20	Ethyl acetate	24	,,	18·70
*iso*Safrol	,,	,,	1·25	Cellulose octaacetate	48	19·90	19·75
Trinitrophenol	,,	20·80	15·80				
Nitrolignin	36	,,	8·0	Ethyl alcohol	,,	,,	13·50
Trichlorophenol	,,	19·90	9·0	Diethyl ether	,,	,,	19·65
Chlorolignin (25·8% Cl)	,,	,,	8·75	Phenyl acetic acid	,,	21·50	21·0
Lignin (by 42% HCl at 20°)	,,	,,	Nil	Tribromophenol	,,	,,	10·20
				Bromolignin	,,	,,	8·75
o-Chlorophenol	30	,,	6·85				

It will be seen from above that hydroaromatic compounds behave just like the aromatic. Also, the only substituent in the benzene ring which does not make it unstable towards ClO_2 is the carboxyl; side-chains are ultimately oxidised to benzoic acid as usual. The behaviour of quinone and hydroquinone is difficult to explain, as the final titre is greater than the original. All double bonds are not unstable, cinnamic acid is stable but not safrol. Furan compounds are very easily decomposed by ClO_2.

Summary.

1. Action of ClO_2 on a large number of organic compounds has been tried and it has been found that all phenolic compounds are readily oxidised by it.

2. Methylated or acetylated phenolic compounds are comparatively more stable towards ClO_2 but not resistant.

3. As lignin contains more than one methoxyl group attached to the benzene ring, the action of ClO_2 on it cannot prove the presence of free phenolic OH in the molecule.

4. Substitutents like Cl, Br or NO_2 make the phenols comparatively more resistant to ClO_2 and as chlorolignin, bromolignin and nitrolignin behave similarly, it is inferred that these enter at least partly the benzene ring in lignin.

5. From the behaviour of methylated or acetylated aliphatic compounds and also that of delignified jute it is concluded that pectin in jute is aliphatic in nature.

6. During delignification, a slow side-reaction takes place with the formation of chlorolignin which has been isolated and examined.

7. The dioxymethylene group is stable towards ClO_2 as also the carboxyl attached directly to the ring. Side-chains are oxidised to carboxylic acids as usual.

The author takes this opportuity to express his deep indebtedness to his teachers Dr. J. C. Ghosh and Dr. J. K. Chowdhury but for whose kind and sympathetic encouragement this work could not have been undertaken. His thanks are due to Prof. S. N. Bose for kindly helping him with criticism and discussion.

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Chemical Examination of the Roots of *Aristolochia Indica*, Linn. Part I.

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Aristolochia indica (Sanskrit, *Rudrajata*; Kannada *Ishwari beru*) is a twining perennial plant growing all over the tropical portions of India. The roots taste very bitter and possess a characteristic aromatic odour. The root and the juice of the fresh leaves are said to be valuable antidotes to the bites of snakes and poisonous insects (Kanny Lall Dey, 'The Indigenous Drugs of India,' 1896, p. 36; Nadkarni, 'The Indian Materia Medica,' 1927, p. 83; Chopra, 'Indigenous Drugs of India,' 1933, p. 566). However, recently Mhaskar and Caius (*Indian Med. Res. Mem.*, 1931.No. 19, pp. 6, 19) have found that according to the technique employed by them, the plant has no antidotal or therapeutic effect against cobra venom.

The isolation of a bitter toxic substance, Serpentarin, from *A. serpentaria* by Chevallier, and a similar one Clemantitin, from *A. clemantitis* by Walz in 1853, may be noted among the earliest chemical studies in this family (Wehmer, 'Die Pflanzenstoffe', 1931, Vol. I, p. 263). These were followed by those of Pohl on *A. rotunda* and *A. clemantitis*. He named the toxic substance Aristolochine and attributed to it the formula $C_{32}H_{29}O_{13}N_2$ (*Brit. Chem. Abs.*, 1892, **1**, 874). Hesse (*Arc. Pharm.*, 1895, **233**, 684) renamed this substance Aristolochic acid, on account of its acidic properties. Its formula was established as $C_{17}H_{11}O_7N$ by Castille (*Chem. Zentr.*, 1922, **III**, 272, 1301), who isolated it from *A. sipho*.

Hesse's work (*loc. cit.*) on the roots of *A. argentina* is of a more detailed character. From the alcoholic extract he was able to obtain in small quantities an amorphous alkaloid to which he reserved the name aristolochine. He was, however, unable to obtain it in a chemically pure form.

Further, from the ethereal extract of the roots he isolated three acids by making use of the differences in the solubil ity of their potassium salts in concentrated potassium hydroxide: aristinic acid, the principal constituent (m.p. 275°; $C_{18}H_{13}O_7N$), aristidinic acid, an isomeric acid containing a methoxyl group (m.p) 260°) and aristolic acid (m.p., 260-70°; $C_{15}H_{11}(_{13})O_7N$). These three acids and aristolochic acid are all more or less yellow compounds

and give dark green solutions with warm concentrated sulphuric acid. This property was taken as indicating their structural relationship. According to Hesse, Serpentarian of Chevallier and Clementatin of Walz are probably identical with aristolochic acid, and aristidinic acid is its monomethyl ether.

In addition to these bitter substances several other compounds such as essential oils, sterols, tannins, etc., have been isolated from different members of the *Aristolochiaceae* (Wehmer, *loc. cit.*).

The only mention in the literature regarding the chemical study of *A. indica* is that of Dymock and Warden ("Pharmacographica Indica", 1893, Vol. III, p. 158). Their work was of a very preliminary character and they obtained indications of the presence of a basic substance and of a brown or yellow resin. Consequently the present investigation was undertaken in order to isolate the constituents and to compare them with those obtained from the other species.

Experimental.

Preliminary investigation.—50 G. of the crushed roots were extracted successively with the following solvents for 24 hours and the extracts dried at 100°

Solvent.	Percentage of extract.
Petroleum ether (b.p. 40-50°)	2·7
Ether	0·9
Chloroform	1·0
Ethyl acetate	0·5
Ethyl alcohol	5·1
Total extractable material,	10·2

500 G. of the powdered roots were subjected to steam distillation and the essential oil content was found to be 0·5%. When tested with Prollius fluid indication of the presence of alkaloidal constituents was obtained. Quantitative estimation showed that it varied between 0·05 to 0·07 per cent. in different samples.* An aqueous extract of

* These values refer to the alkaloidal content of roots obtained from the southern Tamil districts. Those obtained locally round about Bangalore contained only traces.

the roots contained small amounts of starch and reducing sugars and no tannins could be detected.

75 Kg. of carefully picked roots were crushed in a disintegrator and extracted by percolating the material thrice with hot alcohol. The solvent was then distilled off and the concentrated extract was subjected to steam distillation. The volatile constituents came over as a pale yellow oil (130 g.) which had the characteristic odour of the roots. A detailed study of this oil forms the subject matter of the second part.

The semi-solid residue left in the flask was separated from the aqueous layer (A) by decanting off the latter. It was dissolved in alcohol when a small amount of white crystalline material (0·4 g.) separated out. The alcoholic solution was dried on 2 Kg. of the crushed roots and exhaustively extracted with solvents in the order mentioned in the preliminary investigation.

Identification of a phytosterolin.—The solid substance mentioned above was recrystallised several times from large volumes of alcohol when the melting-point rose up to 285-90°. It answered the colour reactions of phytosterols and gave an acetyl derivative melting at 162-63° Its properties indicated that it was probably a glucoside of the type of ipuranol. When hydrolysed by heating with an amyl alcoholic solution of hydrochloric acid according to the method of Power and Salway (*J. Chem. Soc.*, 1913, **103**, 404) a phytosterol, melting at 146°, was obtained. The sugar produced was capable of reducing Fehling's solution, but the quantity was insufficient for the preparation of an osazone.

Aqueous layer Separated from the Semi-solid Residue left after Steam Distillation.

Isolation of an alkaloid aristolochine.—The aqueous layer tasted very bitter and was found to contain a portion of the alkaloidal constituents dissolved probably in the salt form. On the addition of 5%. sodium carbonate the liquid became turbid and a small amount of resinous material also separated out. It was then completely extracted with chloroform.

The chloroform solution was dried over anhydrous sodium sulphate, filtered and extracted with 1% HCl. The solution of the hydrochlorides was boiled with animal charcoal, filtered and the bases reprecipitated by the addition of sodium carbonate. They were again extracted with chloroform and converted into the hydrochlorides.

The aqueous solution was concentrated on a water-bath and finally in a vacuum desiccator. The material crystallised out in the form of a microcrystalline powder. This was filtered, recrystallised and dried at 100°, m. p. 268° (decomp.).

The base liberated from the purified hydrochloride could be readily recrystallised from toluene. After a few recrystallisations it melted with decomposition at 158-159°. However, when attempts were made to recrystallise the substance from methyl alcohol, it dissolved very readily but separated out after a few minutes. This material could then be crystallised only from a large volume of methyl alcohol, m.p. 215°. A similar conversion took place when the original alkaloid was dissolved in absolute alcohol. The substance decom posing at 158° appears to be a molecular compound of the alkaloid with toluene.

It is proposed to call this well-defined chemically individual alkaloid Aristolochine, the name applied to various substances isolated from different species of the *Aristolochiaceae* (Wehmer, *loc. cit.*, Hesse, *loc. cit.*). The complete characterisation of this alkaloid will form the subject of a subsequent communication.

Isolation of allantoin.—The aqueous layer after removal of the alkaloidal constitueuts was treated successively with lead acetate and basic lead acetate. The precipitates obtained were only in very small amounts. Excess of lead was then removed by passing in hydrogen sulphide and the liquid was concentrated under diminished pressure to half the volume.

It was then extracted with amyl alcohol. The amyl alcoholic extract was dried over sodium sulphate and concentrated under diminished pressure. A reddish syrup was obtained which possessed reducing properties. Attempts to isolate chemically individual substances from this proved a failure.

The aqueous solution was further concentrated and the residue obtained in the form of a thick syrup. Treatment of a portion of this with phenylhydrazine yielded glucosazone (m. p. 210°). The material contained hydrolysable sugars. But these could not be separated in a pure condition for purposes of identification.

The syrup was dissolved in absolute methyl alcohol and left in the ice-chest for a few days. A crop of large prismatic crystals separated out slowly. These were collected and crystallised from boiling water (charcoal) as colourless prisms, m. p. 232° (decomp). (Found: C, 30·2; H, 3·9; N, 35·5. $C_4H_6N_4O_3$ requires C, 30·4; H, 3·8; N, 35·4 per cent). Its properties and analytical data indi-

cated that it was allantoin and the melting point was not depressed when mixed with a specimen of pure allantoin prepared from uric acid.

The Petroleum Ether Extract.

This extract consisted of a dark brown oil (1·25 kg.). After keeping it for some days a small quantity of phytosterolin (0·2 g.) separated and was found to be identical with the one already described.

Glycerol.—The oil was saponified and the crude fatty acids were liberated by the addition of dilute sulphuric acid to the soap solution. The aqueous layer was treated with barium carbonate and the filtered solution was concentrated to a small bulk on a water-bath under diminished pressure. The resulting syrup was identified as glycerol by the acrolein test.

The fatty acids were then converted to soap and the soap, sliced into thin shreds, was air-dried and extracted with ether to obtain the unsaponifiable matter. The fatty acids were liberated again and separated into their solid and liquid constituents by the Twitchell method (*J. Ind. Eng. Chem.*, 1921, **13**, 806).

Oleic and linolic acids.—The liquid acids were converted into their methyl esters and the latter were purified by distillation at a pressure of 1 mm. The acids were again liberated and a portion of them was brominated according to the method of Eibner and Muggenthaler. Among the products formed there was no ether-insoluble substance and tetrabromstearic acid (m. p. 113-4°; M. W. 603·0) was isolated. Another portion of the acids was oxidised in alkaline solution by dilute permanganate. The crude mixture of hydroxy acids was washed with a little petroleum ether and then extracted with ether when dihydroxystearic acid (m. p. 131°; M. W. 314) was obtained. The residue was boiled with water and filtered. The acid which crystallised out on cooling proved to be tetrahydroxystearic acid (m. p. 158°; M. W. 347).

Palmitic, stearic, lignoceric and cerotic acids.—The methyl esters (300 g.) of the solid acids were carefully fractionated at 1 mm. pressure:

No. of fraction.	Temperature.	Wt. of the distillate.	Mean M. W. from saponification value.
1	154-164°	165 g.	258
2	164-170°	30	260
3	170-175°	20	270
4	175-182°	15	276
5	182-190°	20	314
Residue	...	50	...

Pure palmitic acid was obtained from the first two fractions (m. p. 62·0°; M. W. 256; m. p. of *p*-phenylphenacyl ester 93·4°). The acid liberated from fractions 3 and 4 after repeated crystallisations from alcohol proved to be stearic acid (m. p. 69°; M. W. 282; m. p. of *p*-phenyl-phenacyl ester 97·8°) and crude lignoceric acid was isolated from the 5th fraction (m. p. 75°; M. W. 368; m. p. of *p*-phenylphenacyl ester 101-2°).

The resinified residue in the flask was dissolved in alcohol, saponified and the dark-coloured acid that separated was dissolved in alcohol and boiled with animal charcoal for several hours. On filtering and cooling, a pale brown slimy material (1 g.) separated. This was filtered and recrystallised several times from alcohol when it came out as a colourless slime (m. p. 78°; M. W. 396). These properties indicate that it is cerotic acid.

Phytosterol and ceryl alcohol.—A reddish brown oil (400 g.) was obtained as the unsaponifiable matter. This had the characteristic odour of the roots and the presence of a small amount of the volatile oil was suspected. Consequently it was subjected to steam distillation. The essential oil was found to be very slightly volatile with steam (5 c. c. passed over with 3 litres of water), and hence the reddish brown oil was distilled in high vacuum and the distillate collected up to 180° was obtained as a pale green oil (90 g.). The residue in the flask solidified to a black mass.

The volatile oil was fractionated into two portions, one boiling at 104-5°/1 mm. (10 g.) and the other (70 g.) at 130-2°/1 mm. (For the chemical study of these, *vide* part II).

The black residue was repeatedly crystallised from boiling alcohol (charcoal) and finally 20 g. of a colourless crystalline material separated out, m. p. 137-8°. It answered the colour reactions of phytosterols and gave an acetyl derivative, m. p. 127°

From the alcoholic mother liquors about 0·5 g. of a colourless slimy material separated out after several days. This substance on several recrystallisations from alcohol melted at 79° (Found: C, 81·5; H, 14·0. Calc for $C_{26}H_{54}O$: C, 81·7; H, 14·2 per cent). Its acetyl derivative melted at 65°. These results indidate that it is ceryl alcohol.

The Ether Extract.

iso*Aristolochic acid.*—As the extraction with ether proceeded a microcrystalline yellow solid separated out from the solvent. The

extraction was stopped after 48 hours although the liquid was still pale yellow in colour.

It could be crystallised from large volumes of alcohol or glacial acetic acid as yellow rectangular plates, m. p. 275° (decomp.), yield 10 g. [Found: C, 59·9; H, 3·4; N, 4·1; M. W. in nitrobenzene (ebullioscopic method) 322. $C_{17}H_{11}O_7N$ requires C, 59·8; H, 3·3; N, 4·1 per cent. and M. W. 341].

This bitter principle is similar to and isomeric with Aristolochic acid (m. p. 215°) isolated by various workers from different species of *Aristolochiaceae* (Wehmer, *loc. cit.*) and consequently it has been named iso*aristolochic* acid.*

The acid is intensely bitter to taste and is very sparingly soluble in the usual organic solvents. The solutions in glacial acetic acid and alcohol show a feeble greenish fluorescence. It dissolves readily in pyridine (a brownish yellow solution) from which it is thrown down on acidification. It dissolves in ammonia, caustic alkalies, alkali carbonates and bicarbonates (dark red solutions). The sodium salt crystallised from water as a dark red powder containing a molecule of water of crystallisation, which is lost only above 150°. (Found: Na, 5·9. $C_{17}H_{10}O_7N.Na, H_2O$ requires Na, 6·04 per cent).

The acid contains neither a methoxyl group (Zeisel) nor a methylenedioxy group (Hans Meyer, "Analyse und Konstitution-Ermittlung Organischer Verbindungen," 1931, p. 497; Sanchez and d' Alessio, *Chem. Zentral.*, 1932, **11**, 257). No indications of the presence of an enolic group were obtained when the substance in alcoholic solution was tested with sodium nitroprusside or tetranitromethane. Estimation of active hydrogen atom was carried out according to the method of Zerewitinoff, suspending the substance in amyl ether. The material gradually formed a deep green solution, and the volume of the gas evolved remained constant after one hour and was equivalent to one active hydrogen atom.

The substance dissolved in boiling acetic anhydride and could be recovered unchanged after one hour. If the boiling was continued, the solution gradually assumed a black colour due to decomposition. No pure product could be isolated from the reaction mixtures. Attempts at acetylation according to several different methods have

* This substance was also found to occur in varying amounts in different samples of the roots. In one experiment 6 g. were obtained from 10 kg. of the roots, and in another 18 g. In the latter case, it is interesting to note that the alkaloid was present only in traces.

so far been unsuccessful. The acid does not react with hydroxylmine, phenylhydrazine or semicarbazide. Further, it has not been found possible to prepare a methiodide. The acid is unaffected when boiled with 50% posassium hydroxide (or 2)% methyl alcoholic potash) for 3 hours. Alkali fusion, however, resulted in considerable resinification, and no definite results could be obtained. With concentrated sulphuric acid, it gives a dark green colouration which changes to brown after addition of a drop of concentrated nitric acid. It is unacted upon by boiling hydrochloric acid, either dilute or concentrated.

Benzoyl iso*aristolochic acid*.—Benzoylation was effected by the Schotten-Baumann method, using potassium hydroxide. Only a small quantity of the derivative separated from the alkaline solution and considerable difficulty was experienced in its purification. Yellow mircocrystalline powder from xylene, m.p. 170-71° (decomp.). (Found: C, 64·9; H, 3·6; N, 3·0. $C_{24}H_{15}O_8N$ requires C, 64·7; H, 3·4; N, 3·2 per cent).

Methyl iso*aristolochic acid*, prepared in the usual manner with methyl sulphate (8 mols.), crystallised from ethyl benzoate in yellow needles, m.p. 267° (decomp.). (Found: C, 61·0; H 3·8; N, 3·9; OMe, 9·1. $C_{18}H_{13}O_7N$requires C, 60·9; H, 3·7; N, 3·9; OMe, 8·7 per cent).

The substance is quite tasteless and is unaffected when refluxed with *N*-methyl alcoholic potash for 4 hours. The product is thus an ether and it follows that iso*aristolochic acid* does not contain a carboxyl group.

Oxidation with hydrogen peroxide: Isolation of an acid of the formula $C_{16}H_{13}O_9N$.—2 G. of *iso* aristolochic acid dissolved in dilute caustic potash (6 g. in 700 c.c. of water) were treated with 9% hydrogen peroxide (31·2 g.) during half an hour at the laboratory temperature (25°). The oxidation was allowed to proceed for 3 hours, with occasional stirring. The exess of hydrogen peroxide was destroyed on the water-bath (1 hour) and the cooled solution was acidified with hydrochloric acid, filtered and concentrated under reduced pressure to one-third the volume. When the concentrated solution was kept in the ice-chest for 18 hours, a slightly reddish solid separated. This was washed with cold water to remove the colouring matter and then repeatedly crystallised from boiling water, when it was obtained as colourless, short, hairy, needles, m.p., 164·5°. [Found: C, 52·0; H, 3·7; N, 3·9; and Eq. wt., 181. $C_{14}H_{11}O_5N$ $(COOH)_2$ requires C, 52·9; H, 3·6; N, 3·9 per cent. and Eq. wt., 182]. It lost 1 molecule of water when kept at 120° for 3 hours.

Further experiments on the constitution of *iso*aristolochic acid are in progress and the results will be communicated in a subsequent paper.

Though Hesse (*loc. cit.*) has isolated three different acidic substances from the roots of *A. argentina*, no other substances similar to iso*aristolochic acid* could be obtained from the roots of *A. Indica*.

The ethereal solution left after filtering off the bitter principle was then extracted with 1% HCl. The amount of alkaloidal material thus obtained was very small and this acid extract was worked up along with the one obtained from the chloroform extract. The ether solution was next extracted with dilute Na_2CO_3 and a small amount of the bitter principle that had remained dissolved in ether was thus recovered. The ether solution was subsequently treated with dilute NaOH, dried over anhydrous sodium sulphate and the ether distilled off. In this manner small amounts of acidic and neutral resinous bodies were obtained. Acid hydrolysis of these did not give any definite results.

The Chloroform Extract.

Here also the bitter principle separated out from solution as the extraction proceeded (13 g.). This was filtered off and washed with a little chloroform. The washings were added to the main extract. The chloroform solution was then extracted with 1% HCl. The hydrochloric acid solution was worked up in the manner described before and the alkaloid obtained here was identical with the one isolated from aqueous layer mentioned in p. 478 Subsequent extractions with Na_2CO_3, gave some more of the dissolved bitter principle. Alkali took up the acidic resin and the neutral product obtained by distilling off chloroform was also found to be a resin. These were non-glucosidic in character.

The Ethyl Acetate Extract.

The bitter principle again separated out during the extraction (17 g.). The solution was distilled and a little more of the bitter principle was recovered. The residue was found to consist of a small amount of a thick reddish resinous material. When this material was boiled with dilute alcoholic hydrochloric acid a small quantity of the bitter principle separated out. Alcohol was distilled over and the neutralised aqueous solution was found to reduce Fehling's solution. Probably the resin contains a glucoside of the bitter principle but this could not be isolated.

The Final Alcoholic Extract.

On concentration and dilution with water a considerable quantity of semi-solid, greyish-black resin separated in an amorphous form. This was soluble in alcohol and alkalies and could be recovered only by reprecipitation. All attempts at its purification proved of no avail. Alkaline and acid hydrolyses were also attempted but without any definite results. The aqueous solution after removal of alcohol by distillation under diminished pressure was examined in the manner described under A. It contained a considerable amount of sugars and from these glucosazone was prepared (m.p. 208°). No glucosidic component could be detected.

Summary.

As a result of the systematic analysis of the roots of *Aristolochia indica* the following substances have been found to occur in it.

1. An essential oil which is responsible for its characteristic odour. This oil consists mostly of high boiling constituents, and owing to its feeble volatility with steam the higher fractions are obtained in the unsaponifiable matter extracted by petroleum ether.

2. The fixed oil is made up of the glycerides of the palmitic, stearic, lignoceric, cerotic, oleic and linolic acids. A considerable amount of sitosterol, a small quantity of the glucoside of phytosterol melting at 146° and ceryl alcohol were isolated from the unsaponifiable matter.

3. The roots are found to contain a very bitter yellow compound sparingly soluble in most of the usual organic solvents. This has the formula $C_{17}H_{11}O_7N$ and is not identical with any of the compounds isolated from other species of *Aristolochiaceae*. It has been named *isoaristolochic acid*.

4. From the basic constituents *Aristolochine*, a new alkaloid, has been isolated as the principal component.

5. The roots have been found to contain considerable amount of reducing sugars from which glucosazone could be readily obtained. Along with these allantoin is found to occur and has been isolated in a pure condition.

We desire to express our thanks to Prof. V. Subrahmanyam of the Biochemistry Department of the Indian Institute of Science and to Dr. M. C. T. Katti, for the large scale extraction of the roots.

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Equilibrium between *n*-Propyl Alcohol, Propyl Ether and Water at 190°.

By N. G. Gajendragad and S. K. K. Jatkar.

No satisfactory data are available for the value of the equilibrium constants of organic reactions in the vapour phase even when reactions of compounds containing not more than three atoms of carbon in a molecule are considered. Amongst such reactions, the production of ethers by the dehydration of alcohols is the least complex and is important from both the technical and physico-chemical point of view. The reactions are:

$$2CH_3OH \rightleftharpoons (CH_3)_2 + H_2O \quad \ldots \quad (i)$$

$$2C_2H_5OH \rightleftharpoons (C_2H_5)_2O + H_2O \quad \ldots \quad (ii)$$

$$2(C_3H_7)_nOH \rightleftharpoons (C_3H_7)_{2n}O + H_2O \quad \ldots \quad (iii)$$

The studies of equilibrium in reactions (*i*) and (*ii*) have already been reported by Jatkar and Watson and Gajendragad, Jatkar and Watson (*J. Ind. Inst. Sci.*, 1126, **9A**, 99; 1932, **15A**, 59). The present investigation concerns itself with studies in equilibrium in reaction (*iii*).

Senderens (*Compt. rend.*, 1909, **148**, 227) prepared propyl ether by passing the vapours of *n*-propanol over alumina catalyst at 250°. Mailhe and Godon (*Bull. Soc. chim.*, 1920, **27**, 121) prepared *n*-propyl ether by passing the vapours of *n*-propyl alcohol over potassium alum dehydrated at 190°. The same reaction at 185°, produced an yield of propyl ether only 54·3% of the theoretical one. This value is considerably lower than the maximum amount obtained by us and the discrepancy is partly due to a faulty method of estimation of propyl ether employed by the authors and partly to the superior activity of our catalyst (*cf.* Jatkar and Watson, *loc. cit.*).

Studies in equilibrium of this reaction have not been done by any previous investigator and are therefore worth investigations from the theoretical point of view. It is also of technical importance since propyl ether is a good substitute for ethyl ether in industry, as the later being a gas in most parts of India is not of much use for industrial purposes.

EXPERIMENTAL.

Propyl alcohol used was distilled at 93·8° at 683 mm. $d_{30}^{30}=0{\cdot}8004$ n_D at 27·2°=1·3835. The same apparatus was used as has been described previously by Gajendragad, Jatkar and Watson (*loc. cit*).

Analysis.—Difficulties were experienced in finding a satisfactory method of analysis of the mixture of propyl alcohol, propyl ether and water. The method finally adopted was essentially as follows. When the run was complete, the entire solution was poured into a 50 c.c. burette. The ether was separated by the addition of saturated salt solution and 50% sulphuric acid added to remove alcohol.

As the method involves loss of ether by vaporization and incomplete separation, corrections must be made to obtain accurate results. In order to measure this loss, the volume of the components recoverable by this method from mixtures of known composition was determined. The corrections were plotted against the true volumes so that by means of the chart, true volume of ether in the mixture could be determined from the observed volume.

The solubility of the pure propyl ether in 50% sulphuric acid was determined with the following results:

(1) Solubility of Pr_2O in H_2O is 0·1% by volume.
(2) Solubility of H_2O in Pr_2O is 0·5% by volume.
(3) Solubility of *n*-propyl ether in 50% sulphuric acid is 75% by volume.

Now starting with pure propyl alcohol and water, mixtures were prepared in a stoppered burette corresponding to various conversions of the propanol. The volume of water separating in each case was noted. Sodium chloride was added, the burette stoppered and shaken and the volumes of the two layers were noted again. The brine layer was separated out and an equal volume of 50% sulphuric acid (equal to the volume of upper layer) was added to the burette, which was then stoppered and shaken several times. The resulting volume of propyl ether (upper layer) is noted. From the observed volumes of propyl ether and the initial volume taken, a graph is plotted.

Starting with 25 c.c. of propyl alcohol, the theoretical volumes of the components at various % conversions are given below in columns A, B and C. The actual total volume of the mixture is given under I. The observed volume of the propyl ether separating is given under E and the correction for the observed volume of propyl ether for 25 c.c. of the total volume is given under F.

TABLE I.

	A	B	C	D	E	F
Corresponding % conversion.	Vol. of Pr_2O.	Vol. of PrOH	Vol. of H_2O.	Actual total vol. of the mixture.	Vol. of Pr_2O.	Correction.
80	18·4	5·0	2·4	26·0	18·4	0·0
70	16·1	7·5	2·1	25·7	15·5	0·5
60	13·8	10·0	1·8	25·4	12·8	1·0
40	9·2	15·0	1·2	25·4	6·2	3·0

Thus in the case of 80% conversion, the observed volume of propyl ether is 18·4 for the total volume 26·0 and on reduction for 25 c.c. total volume, it becomes 17·6 c.c. The correction for the observed volume of propyl ether is then plotted against the reduced volume of 17·6 c.c. for 25 c.c. of the product. This graph is referred to in actual analysis of the product to determine the correction for the volume of propyl ether separating.

Procedure.—Propyl alcohol was run from a burette and the product was collected in exactly the same manner as was done in the case of experiments with methyl alcohol. All the runs taken consist of 25 c.c. of propyl alcohol. This quantity was necessary to reduce the error in the results. Increase in weight of the sulphuric acid bulb, represented the quantity of propylene evolved during the run.

The liquid products were weighed and transferred to a 50 c.c. stoppered gas burette and the volumes of the two layers were noted. The correction to the volume of propyl ether is read on the graph and added to the observed volume and the percentage conversions are calculated on this corrected volume of propyl ether.

The accuracy of the results depends upon the percentage conversions of propyl alcohol because of the large correction necessary at lower conversions. In the vicinity of the equilibrium point, the analysis is accurate within 1%. At and above 80% conversion, the separation of each of the components according to the above method is complete.

Experiments were made to determine the optimum temperature for the reaction. The rate of passage was kept constant at various temperatures and the product was analysed for propyl alcohol, propyl ether, propylene and water. Results are given below.

TABLE II.

Catalyst = Potassium alum (105 g.).

Expt. No.	Temp.	A PrOH converted to Pr_2O.	B PrOH converted to propylene.	PrOH % decomposed. A + B
55-56	190°	69%	0·2%	69·3
53-54	200°	65	2·8	67·8
57-58	210°	75·6	5·0	80·6
59-60	220°	69·0	15·8	84·8
61-62	230°	55·4	28·6	84·0

In order to exclude the side-reaction, the catalyst has to be worked at 190°. Experiments were also tried at 185°, but as could be seen from the comparision of results in Table III, the velocity of reaction at 185° is far slower than the same at 190°.

TABLE III.

Catalyst = Potassium alum (105 g.).

Expt. No.	Temp	Rate of PrOH in c.c. per hour.	Corrected vol. of Pr_2O.	PrOH converted to Pr_2O.
27	185°	0	31·1 c.c.	57%
28	185	20	14·2	62
29	185	20	11·2	55
30	185	20	12·1	58
31	785	10	15·9	69
32	185	10	15·4	67
33	185	5·5	17·4	76
34	185	6	17·5	76
35	190	6	18·0	78
36	190	10	17·4	78
37	190	20	15·0	85

The temperature 190° is therefore the optimum for the reaction. At temperatures higher than 190°, the side-reaction is appreciable, while at lower temperature the velocity of the reaction is slow.

Having determined the optimum temperature, experiments were made to determine the maximum yield of propyl ether. Runs were taken at slow rates over two samples of active catalyst. The results are given in Tables IV and V.

In the following table, the composition of the product in volumes as observed, is given in columns 4, 5 and 6. In the 7th column, the percentage of propyl ether is given and the percentage of propylene amongst the products is shown in the last column.

Experiment No. 43 onwards are the results obtained by passing a mixture $Pr_2O - H_2O$ and under Kp are given the calculated values of

$$\frac{C_{Pr_2O} \times C_{H_2O}}{C^2_{PrOH.}}.$$

TABLE IV.

Catalyst = Fresh active potash alum (100 g.). Temp. = 190°.

Expt. No.	Total wt. of product.	Rate.	Composition of product in volume. Pr_2O.	PrOH.	H_2O.	%Conv.	C_3H_6.
38	20·58	30 c.c.	16·0 c.c.	7·4 c.c.	1·56 c.c.	70·9	0·2%
39	21·18	30	17·1	8·0	1·60	70·1	,,
40	20·67	10	17·6	5·4	2·30	76·2	,,
41	20·39	12	18·8	4·5	2·45	79·3	,,
42	20·33	8·5	19·5	3·1	3·00	82·9	,,

TABLE V.

Catalyst = Fresh potash alum (100 g.). Temp. = 190°.

Expt. No.	Total wt. of distillate.	Rate.	Composition of product in mols. % PrOH.	H_2O.	Pr_2O.	% Conv. Pr_2O	C_3H_6.	Kp.
47	17·38	7·5 c.c.	13·03	46·8	40·1	89·2	1·1%	11
48	18·00	8·6	14·80	22·1	41·5	82·0	0·6	8
49	18·58	6·5	12·10	47·1	40·7	83·6	1·6	13
50	18·68	6·0	13·20	46.4	40·4	84·1	1·6	10
51	19·78	11·0	15·20	42·8	41·9	42·2	1·1	8

The reverse reaction was studied with the following arrangement of apparatus. Propyl ether was dropped under a controlled rate from the burette into a bulb wherein it was vapourised, then the vapours were allowed to be saturated with water in the copper saturator and finally the vapours were freed from spray by the trap. The bulb, copper saturator and the trap were completely immersed in a a thermostat at 88°−89°. The vapours, thus saturated, were then passed through the apparatus and the product was analysed for propyl ether, propyl alcohol, water and propylene as in the direct runs.

TABLE VI.

Reverse reaction on the same catalyst.

Expt. No.	Total wt. of product.	Rate.	Composition of product in volume.				
			Pr_2O.	PrOH.	H_2O.	Pr_2O.	C_3H_6.
43	16·60	4·4 g.	16·5 c.c.	2·22 c.c.	2·22 c.c.	39·0%	0·1%
44	16·51	2·0	16·8	2·40	1·80	87·3	„
45	18·20	6·0	18·1	2·55	2·48	88·4	„

DISCUSSION.

If the percentage conversions given in Table IV are plotted against the rates, the curve cuts the zero rate at 84% conversions. The equilibrium constant corresponding to this value is about $Kp=8$. If values of Kp as calculated from the results of the reverse reactions given in Table VI, are plotted against the rates, the extrapolation gives the value of $Kp=8$.

By starting with a fresh sample of the active catalyst, we could actually get 84% conversion as in Table IV, Expt. 50.

Experiments were incidentally undertaken to study the mechanism of catalytic dehydration. Although there is a large volume of similar work of Sabatier and his school of workers, no exhaustive study of particular cases has so far been made. It is usually assumed that the dehydration occurs in two steps:

$$2C_nH_{2n+1}OH \longrightarrow (C_nH_{2n+1})_2O + H_2O$$

and $$(C_nH_{2n+1})_2O \longrightarrow 2C_nH_{2n} + H_2O$$

the second reaction predominating at higher temperatures.

In the case of ethyl alcohol Senderens (*Ann. chim. phys.*, 1912. *viii*, **25**, 505) believes that the formation of ether and ethylene from alcohol are two independent reactions. He found that at 250°, the rate of decomposition of pure ether to give ethylene is many times greater than the rate of formation of ethylene from alcohol and with some catalysts and other alcohols, the formation of ether was insignificant. Ether may not be therefore be an intermediate product in the dehydration. The following experiments point to similar conclusion in the case of propyl alcohol, propyl ether having been found to be more stable than propyl alcohol under the action of catalyst.

TABLE VII.

Decomposition of propyl ether.

Expt. No.	Temp.	Rate.	% Conv. to C_3H_6.
63	230°	10 c.c.	46·7
64	230	5	67·5
65	230	10	46·7
66	210	10	46·9
67	190	10	1·2
68	190	10	0·4

Experiments 63-68 were made by passing propyl ether over the catalyst. The results when compared with Table I bring out the comparative stability of ether compared with alcohol when allowance is made for the catalyst being engaged in decomposing the alcohol. Further it was found that part of propyl ether was converted to propyl alcohol, the reverse reaction taking place with the water formed by decomposition of ether.

The following experiments 69 to 71 were then undertaken to find the extent of decomposition by passing mixtures of propyl alcohol and propyl ether. In order to have the same time of contact, this mixture was passed at twice the rate of pure ether was passed. If we assume that propylene comes from propyl ether then we ought to get two molecules of propylene to one molecule of water. On the other hand propyl alcohol on decomposition would give propylene and water in the ratio of one to one. The results show that the latter relation holds good. Further propyl ether does not affect the direct dehydration of propyl alcohol to propylene.

TABLE VIII

Rate = 20 c.c. an hour. Temperature = 230°.

Expt. No.	Composition of initial mixture.		Composition of final mixture.			
	Pr_2O.	PrOH.	Propylene.	H_2O.	Pr_2O.	PrOH.
69	7·55 g.	4·45 g.	1·84 g.	1·75 g.	7·00 g.	1·40 g.
70	7·50	5·89	3·14	1·55	7·55	1·16
71	9·33	5·51	3·90	1·75	7·40	1·40

SUMMARY.

1. The equilibrium in the reaction $2n\text{PrOH} \rightleftharpoons n\text{Pr}_2\text{O} + \text{H}_2\text{O}$ at 190° corresponds to 84% conversion of the alcohol.

2. Propyl ether cannot be the intermediate product in the dehydration of propyl alcohol to propylene because propyl ether is found to be far more stable than propyl alcohol to the action of potassium alum catalyst.

Our thanks are due to Dr. H. E. Watson for helpful guidance during the course of the investigation.

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Chemical Examination of the Roots of *Aristolochia Indica*, Linn. Part II. The Essential Oil.

By U. S. Krishna Rao, B. L. Manjunath and K. N. Menon.

This paper deals with the study of the essential oil (163 g.) obtained from the roots of *Aristolochia indica* during the systematic investigation described in the previous part. The pale yellow oil which separated from the aqueous layer in the steam distillate was dried over anhydrous magnesium sulphate and used for the determination of the physical and chemical constants.

$D_{4}^{31°}$	0·9525	Acid value	2·0
$\eta_{D}^{31°}$	1·5023	Ester value	7·3
$\alpha_{D}^{31°}$	−33·11°	Ester value after acetylation	22·5

The oil possessed the characteristic aromatic odour of the roots. When cooled to −15° it became a viscous liquid strewn with a few crystals. The oil dissolved in 5 volumes of 95% alcohol and was found to be practically insoluble in 70% alcohol. A portion of the oil was subjected to fractional distillation under diminished pressure (1 mm.); only a small fraction came over below 100° and over half the quantity was collected between 100° and 116°. The higher fractions up to 150° were in small amounts.

The oil did not contain any substance possessing the phenolic or the lower alkoxy groups. The carbonyl compounds estimated according to the bisulphite method amounted to 3%

The total quantity of the essential oil (150 g.) was dissolved in water and extracted with 5% sodium bicarbonate solution. The amount of free acids thus extracted was found to be too small to permit of any investigation. The oil was recovered from the ether solution and shaken for 48 hours with excess of a saturated solution of sodium bisulphite. The bisulphite extract was separated and hydrolysed by boiling with sodium carbonate. The liberated compounds were extracted with ether and the ether extract, dried over anhydrous magnesium sulphate, gave a small quantity of an oil

possessing the odour of *iso*vaniliin. Attempts to prepare a semicarbazone proved unsuccessful.

The oil was then boiled under reflux with excess of 0·5 *N*-alcoholic potash to saponify the ester constituents. Alcohol was distilled off after one hour, and the alkaline solution was separated from the oil. On acidifying the former, a viscous oil was obtained. This was separated into solid and liquid constituents by Twitchell's method. The former on crystallisation from alcohol melted at 61° and was recognised as palmitic acid (M. W. 254, mixed m.p. with pure palmitic acid 61·5°). The liquid portion (M.W. 286) did not give any solid product when brominated according te Eibner and Muggenthaler and on oxidation with dilute permanganate was converted into dihydroxystearic acid (m.p. 136°; M.W. 316°). Thus the presence of oleic acid in it was established.

The oil (130 g.) was then subjected to fractional distillation under dimished pressure using a four pear Young column and the following fractions were collected:

Fraction.	Temperature.	Wt. of fraction.
1	42-44°/5 mm.	2·6 g.
2	110-115°/1 mm.	10·7
3	118-130°	72·6
4	130-140°	16·0
5	140-150°	13·7
6	150-160°	8·3
	Residue and loss	6·1

A small amount of crystalline material separated from the first fraction. This substance also separated out from the second fraction on cooling in the refrigerator. When recrystallised from alcohol, it had the characteristic odour of camphor, m.p. 176°, and did not depress the m.p. of pure camphor. Further examination was not possible owing to the insufficiency of the material.

The fractions 2 to 6 were subjected to very careful and repeated fractional distillations under a pressure of 1 mm. In this manner two principal fractions were obtained, A (75 g.) boiling at 104-05° was colourless, and B (15 g.) boiling at 128-30° was pale green.

Isolation of a new Sesquiterpene—Ishwarene.

Several unsuccessful attempts were made to refractionate A by distilling it at different pressures. Finally it was repeatedly distilled over sodium till all the compounds containing oxygen were eliminated. The purified substance was a mobile colourless liquid and analysis showed that it was a new sesquiterpene, b.p. 130-132°/10 mm.; 104-105°/1 mm. D_{15}^{15} 0·9227 ; η_D^{25} 1·5035 ; α_D^{25} −42·37° and the name *Ishwarene* is proposed for it. [Found: C, 88·2; H, 12·0; M.W. (cryoscopic method in benzene), 204. $C_{15}H_{24}$ requires C, 88·2; H, 11·8 per cent. and M.W. 204].

The hydrocarbon gave a liquid monohydrochloride [b.p. 128-30°/ 1 mm.; $d_{30}^{30°}$ 1·0200; $\eta_D^{30°}$ 1·5107 ; $[\alpha]_D^{30°}$ in alcoholic solution −18·7°]. (Found: Cl, 14·8. $C_{15}H_{24}$, HCl requires Cl, 14·7 per cent). When attempts were made to prepare the nitrosite, nitrosate, nitrosochloride and the additive compound with bromine, oily products were obtained which could not be purified.

To gain some insight into the structure of this sesquiterpene, attempts were made to dehydrogenate it by heating with selenium for 48 hours at 260-270°. A dark blue liquid was formed. This was distilled over sodium and the distillate carefully fractionated. Most of the original material was recovered unchanged. The smaller fractions and residue did not give any derivatives with picric or styphnic acids.

Isolation of a New Sesquiterpene Ketone—Ishwarone.

The pale green fraction B was obtained in large quantity (60 g.) from the unsaponifiable matter extracted by petroleum ether, from the residues left after the steam distillation of the total alcoholic extract of the roots (*vide* Part I). The oil was highly viscous and the green colour partially disappeared on keeping it exposed for a few days. Unsuccessful attempts were made to fractionate it further by redistilling it at various pressures.

Preliminary tests indicated the presence of a ketone. Fraction B was then dissolved in excess of 95% alcohol and excess of semicarbazide hydrochloride and sodium acetate were added and the mixture refluxed for 2 hours. The semicarbazone separated as a solid (50 g.).

This was filtered off and recrystallised from alcohol in silky white needles, m. p. 240°. (Found: C, 69·7; H, 9·1 ; N, 15·5. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·1; N, 15·5 per cent).

The semicarbazone was decomposed by refluxing it with 10% oxalic acid and the liberated ketone was purified by steam distillation. The product was dried and distilled when almost the entire quantity passed over at 118-20°/1 mm. as a fairly mobile colourless liquid. The substance had the following constants: $d^{30°}_{30°}$, 1·0290 ; $\eta^{30°}_{D}$, 1·5122. $\alpha^{30°}_{D}$,—46·47°.

Analysis showed that it was a sesquiterpene ketone of the formula $C_{15}H_{22}O$ and the name *Ishwarone* is proposed for it. [Found: C, 82·5 ; H, 10·0 ; M. W. (cryoscopic in bromoform), 214. $C_{15}H_{22}O_4$ requires C, 82·6 ; H, 10·1 per cent and M. W. 218]. Its semicarbazone was identical with the one prepared from the fraction B. The p-*nitrophenylhydrazone* crystallised from alcohol in yellow plates, m. p. 186·5°. (Found: N, 11·8. $C_{21}H_{27}O_2N_3$ requires N, 11·9 per cent). The 2:4-*dinitrophenylhydrazone* crystallised from alcohol in long yellow silky needles, m. p. 167·5°. (Found: N, 14·1. $C_{21}H_{26}O_4N_4$ requires N, 14·1 per cent).

When it was attempted to prepare the oxime by the usual methods a white crystalline compound was obtained which was insoluble in alkalies. On crystallising it from methyl alcohol it was obtained pure and melted sharply at 133°. (Found: C, 77·3; H, 9·9; N, 6·1. $C_{15}H_{23}ON$ requires C, 77·3; H, 9·9; N, 6·0 per cent). The substance was found to contain 1 active hydrogen atom (Zerewitinoff method) and is probably an iso*oxime*.

Isolation of a Sesquiterpene Alcohol—Ishwarol.

The residues from the fraction B (30 g.) after the complete removal of the semicarbazone of Ishwarone were distilled under diminished pressure ; 15 g. of the distillate were collected, the rest having resinified. This was carefully fractionated under a pressure of 1 mm.

Fraction.	Temperature.	Quantity.	$\eta^{25°}_{D}$.
1	up to 126°/1 mm.	4 g.	1·5114
2	126–28°	7	1·5126
3	128–30°	3	1·5148

The middle fraction on redistillation gave a pale yellow viscous oil which was found to be a new sesquiterpene alcohol *Ishwarol*, of the formula $C_{15}H_{23}.OH$, $d_{30°}^{30°}$, 0·9926; $\eta_D^{30°}$, 1·5098; $\alpha_D^{30°}$ (in alcohol) −7·29°. [Found: C, 81·9; H, 11·1; M. W. (cryoscopic in bromoform), 219; one active hydrogen atom (Zerewitinoff method). $C_{15}H_{23}OH$ requires C, 81·8; H, 11 0 per cent. M. W., 220].

The alcohol did not react with phenyl *iso*cyanate and resinified when heated with phthalic anhydride. However, it was partially acetylated on boiling with acetic anhydride and sodium acetate for a period of 3 hours.

Summary.

The essential oil obtained from the roots of *Aristolochia indica* has been found to consist mainly of new sesquiterpenoid compounds. A small quantity of camphor was also found to occur in it. A sesquiterpene *Ishwarene*, a sesquiterpene ketone *Ishwarone*, and a sesquiterpene alcohol *Ishwarol*, have been isolated and described. The names are derived from the Kannada name of the roots, *Ishwari beru*

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Viscosity of Dilute Solutions of Non-electrolytes.

By Balabhadra Prasad.

A good deal of work has been done on the viscosity of solutions of non-electrolytes, but few workers have used solutions below tenth molal. Various formulæ connecting viscosity and concentration have been proposed (Dunstan and Thole, "Viscosity of Liquids," page 43), but all these relate to moderately concentrated solutions, where the laws of dilute solutions are not applicable.

In the Landolt-Börnstein's tables, viscosities (η) of 1 and 5 % sucrose sclutions are given for a number of temperatures. By applying the laws of dilute solution, the vapour pressure (p) of any solution is calculated at the temperature at which the viscosity is measured. It is found that the following relationships hold between the viscosity and vapour pressure of the solutions concerned:—

$$\log \eta = -0{\cdot}365 \log p - 1{\cdot}52 \text{ for the 1 \% solution} \quad \ldots \quad (i)$$

$$\log \eta = -0{\cdot}358 \log p - 1{\cdot}49 \text{ for the 5 \% solution} \quad \ldots \quad (ii)$$

It is quite well known (Porter, *Phil. Mag.*, 1912, **23**, 458) that viscosity (η_0) and vapour pressure (p_0) of water are connected together by the equation,

$$\log \eta_0 = -0{\cdot}362 \log p_0 - 1{\cdot}54 \quad \ldots \quad (iii)$$

All the three equations are straight line equations and can be represented by $y = mx + k$, where m and k are different for the different equations. The differences between the m and k values for water and the 5 % solution are large, but then it has to be borne in mind that laws of dilute solution have been applied for calculating the m and k values for the solution which is by no means a dilute one. The difference between the m values of water and the 1 % solution is 0·8 % and that between the k values 1·3 %. *Assuming that in still more dilute solutions they would disappear, the two equations (the*

one for the solution and the other for the solvent) could be combined to give the equation,

$$\log \eta/\eta_0 = -0{\cdot}362 \log p/p_0 \qquad \ldots \quad (iv)$$

which after substituting $1-n/N$ (n = number of gram moleculeles of the solute in N gram molecules of the solvent) for p/p_0 and expanding, assumes the form (the higher power are neglected because of dilution),

$$\eta/\eta_0 = 1 + 0{\cdot}362\, N/n \quad \text{or} \quad \eta/\eta_0 = 1 + \alpha C$$

where $\alpha = 6{\cdot}52 \times 10^{-3}$ if concentration (C) is measured in gram molecules per litre.

In order to test this equation and consequently the assumption made, viscosity of aqueous solutions of sucrose and fructose were measured at 30°, 35° and 40° and of glucose at 35° and 40° for a number of concentrations.

Experimental.

The thermostat used for the experiment was electrically heated and the temperature was controlled by means of a toluene thermo-regulator. The thermostat had a glass window for making observations. It could be lighted when necessary by means of a 25 watt lamp which was kept immersed in the water of the thermostat. The stirring was done electrically. The temperature could be maintained within 0·005°.

Viscosity was measured by means of Ostwald's viscometer. The viscometer was always clamped at the same place. A piece of thread was stretched over the thermostat. After clamping, the viscometer was rotated till the middle part of the wider arm and the edge of the narrower arm, which had a rubber tube attached to it, were in a line with the thread. This procedure ensured that the viscometer was always placed in the same position. Three marks were made; one above the bulb on the capillary side, one below the bulb on the same side and the third above the bulb in the wider limb. The viscometer was so constructed that after the liquid flowed back, it rested in the capillary tube two and half inches below the lower mark on the capillary limb. The liquid in the wider limb was made up to the mark above the bulb in the limb, the liquid in the other limb resting in the capillary tube itself. This ensured that the volume of the liquid taken was the same in every case.

Three to five readings for time were taken in case of every solution. They seldom differed from one another by more than 0·2 seconds. The mean of the time was used in calculating viscosity. Every time, the time of flow for a solution was measured, the same for the water used, was also measured. In case of every solution the weight of the solution, contained in a specific gravity bottle at the temperature concerned, was found to the third place of decimal. η/η_0 was calculated by the formula; $\eta/\eta_0 = tw/t_0w_0$ where t and w denote the time of flow and the weight of the said volume of the solution respectively and t_0 and w_0 the same for pure water. No kinetic correction was considered necessary as (*i*) the time of flow was quite large, (*ii*) the bore of the capillary tube was 0·36 mm. only and (*iii*) time taken by water and solutions did not differ much from each other on account of the solutions being dilute.

In the following tables, C, η/η_0 and α are given for the various solutions.

TABLE I.

Sucrose solutions.

	30°		35°		40°	
$C \times 10^3$.	η/η_0.	α.	η/η_0.	α.	η/η_0.	α.
2·339	1·0017	0·727	1·0016	0·684	1·0022	0·941
4·678	1·0034	0·727	1·0037	0·791	1·0039	0·834
7·018	1·0053	0·755	1·0056	0·798	1·0053	0·755
9·357	1·0072	0·769	1·0077	0·823	1·0077	0·823
11·696	1·0086	0·735	1·0089	0·761	1·0092	0·787
14·035	1·0101	0·720	1·0111	0·790	1·0116	0·827
16·374	1·0131	0·800	1·0129	0·788	1·0127	0·776
18·714	1·0159	0·849	1·0141	0·748	1·0145	0·775
21·053	1·0178	0·846	1·0177	0·841	1·0168	0·798
	α Mean = 0·780		α Mean = 0·770		Mean value of α for the last eight figures = 0·797	

Table II.

Fructose solutions.

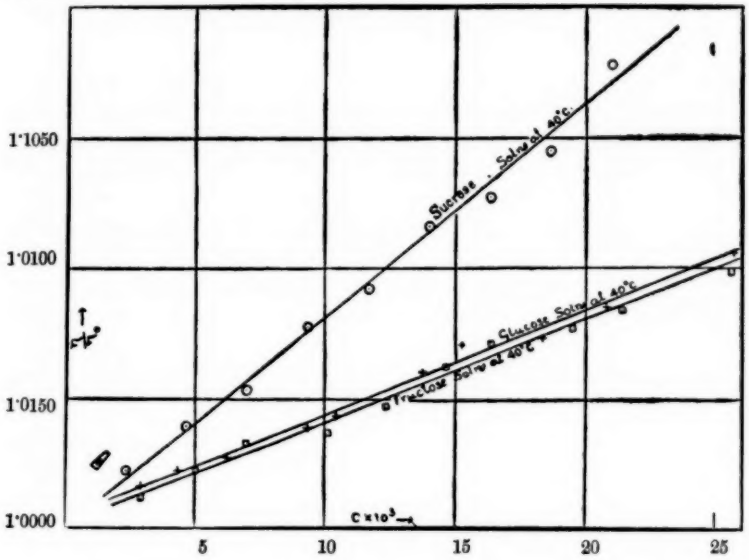
30°			35°			40°		
$C \times 10^3$.	η/η_0.	α.	$C \times 10^3$.	η/η_0.	α.	$C \times 10^3$.	η/η_0.	α.
2·484	1·0011	0·443	2·293	1·0008	0·350	2·947	1·0012	0·407
4·627	1·0022	0·475	3·964	1·0020	0·505	5·067	1·0022	0·434
7·409	1·0031	0·418	6·729	1·0025	0·372	7·000	1·0033	0·471
9·058	1·0038	0·419	8·462	1·0038	0·449	10·142	1·0037	0·365
12·562	1·0054	0·430	11·831	1·0049	0·414	12·387	1·0047	0·379
15·344	1·0066	0·430	15·324	1··064	0·418	14·684	1·0052	0·422
17·800	1·0077	0·433	16·444	1·0071	0·432	16·418	1·0071	0·432
20·238	1·0090	0·445	19·196	1·0078	0·406	19·556	1·0077	0·394
22·724	1·0097	0·427	20·755	1·0082	0·395	21·441	1·0084	0·392
26·756	1·0112	0·419	22·804	1·0090	0·395	25·667	1·0099	0·386
Mean value of $\alpha = 0·434$			Mean value of $\alpha = 0·414$			Mean value of $\alpha = 0·408$		

Table III.

Glucose solutions.

35°			40°		
$C \times 10^3$.	η/η_0.	α.	$C \times 10^3$.	η/η_0.	α.
2·969	1·0016	0·539	2·127	1·0013	0·611
4·342	1·0022	0·507	4·000	1·0022	0·550
6·240	1·0027	0·433	7·111	1·0032	0·450
9·347	1·0039	0·417	9·160	1·0039	0·426
10·484	1·0043	0·410	11·480	1·0052	0·453
13·751	1·0060	0·436	13·658	1·0060	0·439
15·31*	1·0070	0·451	15·853	1·0068	0·429
18·387	1·0073	0·397	18·124	1·0074	0·408
20·849	1·0085	0·408	20·271	1·0085	0·419
25·715	1·0106	0·412	24·453	1·0104	0·425
Mean value of $\alpha = 0·441$			Mean value of α for the last nine figures only $= 0·444$.		

In the following figure η/η_0 is plotted against concentration for the solution of each of the solutes at 40°. The values for other temperatures also behave in the same way.



It is evident from the tables as well as the diagram that a is fairly constant for any solute. Its variation with temperature is within experimental error. Even if it varies with temperature, the variation is not very marked. However it is not independent of solute thus conclusively proving that the assumption made in deducing equation (*iv*) is wrong.

Summary.

1. The viscosity of dilute solutions of sucrose and fructose has been measured at 30°, 35° and 40° and of glucose at 35° and 40°.

2. All these viscosities can be represented by the equation $\eta/\eta_0 = 1 + aC$ where a is independent of temperature, but not of the solute.

3. The value of a for sucrose solutions is about 0·78, fructose 0·42 and glucose 0·44.

4. The concentration range is 2×10^{-3} to 27×10^{-3} g. molecules per litre.

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Action of Hydrogen Sulphide on Insoluble Chromates, Part I. Lead Chromate and Silver Chromate.

By H. B. Dunnicliff and Brahm Prakash.

Dunnicliff and Soni (*J. Phys. Chem.*, 1929, **33**, 81) showed that hydrogen sulphide decomposes potassium chromate with the formation of chromium hydroxide, sulphur, potassium thiosulphate and potassium polysulphide. Dunnicliff and Kotwani (*ibid.*, 1931, **35**, 3214) showed that, on similar reduction, chromic acid gives chromium sulphate, chromium thiosulphate, chromium hydroxide and sulphur.

When hydrogen sulphide is passed through a suspension of freshly precipitated lead chromate in water, the orange colour first changes to dull brown and then through various shades until, after about 24 hours, a greenish black solid residue is formed. The neutral filtrate and washing contained no sulphur acid except hydrogen sulphide.

The precipitate contained lead sulphide, chromium sulphate, and thiosulphate (partly co-ordinated), chromium hydroxide, sulphur and unattacked lead chromate. Particular care was taken in testing for sulphurous and thionic acids, which were, however, absent.

When analysed by the method shown on page 509, it was found that, at laboratory temperature (15-20°), only about 5% of the lead chromate were decomposed while, at 80-85°, 15-20% were attacked. Grinding the chromate in a mechanically operated agate mortar, increased the decomposition to about 30% and a slight further increase was obtained by passing hydrogen sulphide through a suspension of freshly precipitated lead chromate in 3 litres of water.

This showed that, if lead chromate could be obtained in a sufficiently fine state of devision, complete interaction might be effected.

A suspension of 1 g. of lead chromate was obtained in 2 litres of water by mixing 1 litre each of potassium chromate and lead chloride in stoichiometric proportions. The hydrolysis of the lead chromate so produced was shown not to be excessive by a determination of the p_H value of the solution by the Comparator-indicator method. It was then mixed with about 4 litres of water saturated with hydrogen sulphide and allowed to stand overnight. Filtration was tedious and this is an important factor affecting the ultimate result. By this method, 90-95% of lead chromate were attacked.

Experimental.

Co-ordinated and Ionic Sulphate.

(*i*) The precipitate was transferred to two separate filter papers (*a*) and (*b*). One part (*a*) was extracted with 0·3*N*-KOH, which removes thiosulphate, sulphate and a portion of the led chromate.

$$PbCrO_4 + 4\,KOH = K_2PbO_2 + K_2CrO_4 + 2H_2O.$$

An aliquot portion of this extract was treated with barium chloride solution to precipitate sulphate and chromate. This precipitate was filtered on a weighed filter paper and washed with dilute hydrochloric acid, which dissolved out barium chromate, leaving barium sulphate unaffected. The weight of $BaSO_4$ indicates the total sulphate present. The chromic acid liberated was a measure of the unused lead chromate in that portion. The rest of the original precipitate (*a*) was extracted with HCl-NaCl solution (100 c.c. of a saturated solution of sodium chloride, 15 c.c. of water and 10 c.c. of concentrated hydrochloric acid, *d* 1·19), the unattacked lead chromate dissolved liberating an equivalent amount of chromic acid, which was a measure of the unattacked lead chromate present.

(*ii*) The second portion of the precipitate (*b*), was directly extracted with HCl-NaCl solution and lead and sulphate estimated in it. A little sulphate would be formed by the oxidation of thiosulphate to sulphate by chromic acid solution but, as the decomposition was 95% or more, the amount of sulphate so formed was relatively small.

The results in Table I show that the amounts of sulphate in the second determination (*b*), are much less than those found in the first (*a*), indicating that the sulphate is present in both the ionic and co-ordinate forms.

Table I.

Determination of the state of combination of the sulphate group in the final precipitate.

Hydrogen sulphide is passed into $PbCrO_4$ suspended in water at laboratory temperature and about 10% of the chromate is attacked.

	a Total (SO_4) for 1 g. Pb (KOH-extract).	*b* Ionic (SO_4) for 1g. Pb (HCl-NaCl-extract).	*a*/*b*.
1.	0·2043 g.	0·0767 g.	2·66
2.	0·3499	0·1476	2·37

Precipitates were ultimately analysed as follows:—

(*a*) The precipitate was extracted with 0·3*N*-KOH (approx.) and as a pale yellow liquid obtained in which sulphate, thiosulphate and unused chromate were estimated (Dunnicliff and Kotwani, *loc. cit.*).

(*b*) The residue after this extraction was treated with 5% sulphuric acid containing a little alcohol to extract chromium hydroxide as sulphate. The hydroxide was reprecipitated with ammonia and weighed as Cr_2O_3. Chromate was estimated after filtering off the chromium hydroxide.

(*c*) The residue from (*b*) was extracted with cold HCl-NaCl solution and any lead chromate still left, was determined as chromic acid. Direct extraction with NaCl-HCl solution which removes Pb as well as Cr_2O_3 is not feasible as it is not possible to estimate the Cr_2O_3 quickly in presence of the lead.

Table II gives the results of chromic oxide estimation in which residues of unattacked chromates are represented by the sum of the amount of chromate found in the three extracts, *a*, *b*, *c* (*vide supra*).

TABLE II.

Estimation of chromic oxide.

Started with lead chromate (1 g.).

Expt.	Wt. of unattacked lead chromate.	Lead chromate attacked.	Chromic acid present as hydroxide, sulphate and thiosulphate.	
			Expt.	Theory.
1. (*a*)	0·0544 g.			
(*b*)	0·0163	92·47%	0·2154 g.	0·2176 g.
(*c*)	0·0046			
	0·0753			
2. (*a*)	0·0375			
(*b*)	0·0163	94·62	0·2220	0·2225
(*c*)	0·0000			
	0·0538			
3 (*a*)	0·0326			
(*b*)	0·0109	94·51	0·2220	0·2224
(*c*)	0·0114			
	0·0549			

Free sulphur was determined by oxidising all the sulphur products to sulphate with sodium peroxide and estimating the sulphate in excess of that obtainable from thiosulphate, sulphate and lead sulphide, as determined directly.

The results given in Table II are calculated as follows, mean values being used to illustrate the method. Assuming the reactions,

$$PbCrO_4 + H_2S = PbS + H_2O + CrO_3$$

$$2\ CrO_3 + 3H_2S = Cr_2O_3 + 3H_2O + 3S \qquad \ldots\ (i)$$

48 g. sulphur $\equiv$ 323·2 g. $PbCrO_4$.

Also, on the assumption that hydrogen sulphide is oxidised to sulphate by the chromic acid produced.

$$3H_2S + 8CrO_3 = Cr_2(SO_4)_3 + 3H_2O + 3Cr_2O_3 \qquad \ldots\ (ii)$$

36 g. $(SO_4) \equiv 323{\cdot}2$ g. $PbCrO_4$

8·554 g. $(SO_4) \equiv 76{\cdot}81$ g. $PbCrO_4$.

The following reactions involving the formation of thiosulphate are assumed:—

$$8CrO_3 = 4Cr_2O_3 + 12(O)$$

$$6H_2S + 12(O) = 3H_2S_2O_3 + 3H_2O \qquad \ldots \qquad \ldots\ (iii)$$

42 g. $(S_2O_3) = 323{\cdot}2$ g. $PbCrO_4$

2·344 g. $(S_2O_3) \equiv 18{\cdot}04$ g. $PbCrO_4$

The values for sulphate and thiosulphate, calculated for 100 g. of chromic acid from lead chromate, are about 3% higher than those obtained in the case of the reduction of chromic acid by hydrogen sulphide (Dunnicliff and Kotwani, *loc. cit.*) suggesting that the chromic acid obtained from $PbCrO_4$ is a more active oxidising agent and perhaps this is explainable from its method of formation.

In view of the fact that six to seven litres of water had to be used for these experiments, the extremely high values for sulphur are possibly due to the oxidation of hydrogen sulphide by the oxygen dissolved in water and taken up from the atmosphere and, to a minor degree, to photochemical action.

Oxygen dissolved in water was estimated by Winkler's method (*Ber.*, 1888, **21**, 2843; *cf.* also *Z. anal. Chem.*, 1914, **53**, 665; *C.F.C.A.*,

1915, **8**, 674) and it was shown that this oxygen alone is sufficient to account for the excess of sulphur formed in the reaction.

TABLE III.

Values calculated for 100 g. of lead chromate actually attacked.

Expt.		1 g.	2 g.	3 g.	4 g.	5 g.
1.	Thiosulphate (S_2O_3)	2·3530	2·3729	2·3439	2·3080	2·3440
	In terms of 100 g. of lead chromate (Eqn. 3, v.s.)					18·04%
2.	Sulphate (SO_4)	8·6260	8·5550	8·5610	8·4740	8·5540
	In terms of 100 g. of lead chromate (Eqn. 2, v.s.)					76 81%
3.	Sulphur (S) in the free state.	2·50	2·11	2·85	4·40	0 76 (Theory).
	In terms of 100 g. of $PbCrO_4$ (Eqn. 1, v.s.)					5·15 (by difference).
4.	Chromic oxide (Cr_2O_3)	23·54	23·50	23·46	...	23 50
	In terms of 100 g. of $PbCrO_4$					99·90%

Final greenish-black precipitate at 10°.

In various experiments performed under identical conditions, sulphate was estimated in the final precipitate both in the alkali and the HCl-NaCl extracts to see whether it was co-ordinated (Table IV). Lead chromate was treated in its finest state of division and about 95% were actually attacked.

TABLE IV.

Expt.	$BaSO_4$ by HCl acid treatment. (*a*)	$BaSO_4$ by KOH treatment. (*b*)	Ratio *b* : *a*.
1.	0·0279 g.	0·1767 g.	6·30 : 1·00
2.	0·0289	0·1767	6·28 : 1·00
3.	0·0290	0·1767	9·90 : 1 00

A comparison of the results with those shown in Table I indicates that, as the percentage of lead chromate decomposed increases, the precipitate undergoes further changes, resulting in the co-ordination of more sulphate at the expense of ionic sulphate. It is possible that,

when the lead chromate is quantitatively attacked, the whole of the sulphate might be co-ordinated.

Ignoring the values for sulphur, the analyses in Table III (slow reaction: H_2S on suspension at ordinary temperature) work out to the following equation:—

$$21(3H_2S+2PbCrO_4)=42PbS+4Cr_2(SO_4)_3+Cr_2(S_2O_3)_3+3S+32Cr(OH)_3+15H_2S.$$

The effect of temperature.—When the reactants were mixed at 50° and 70°, the reaction was found to proceed much more rapidly. Estimations of sulphate and thiosulphate in the precipitate were carried out after extraction with potassium hydroxide. A comparison of the results with those shown in Table II, indicates that

(*i*) The slower the reaction, the greater the tendency to form thiosulphate.

(*ii*) Possibly some sulphate is formed by the oxidation of thiosulphate.

(*iii*) The greater activity of chromic acid produced from lead chromate is again emphasised.

TABLE V.

Final greenish-black precipitate.

Values are calculated per 100 g. of lead chromate actually attacked.

Expt		1 g.	2 g.	3 g.	4 g.	In terms of 100 g. $PbCrO_4$.
	Temperature = 50°.					
1	Thiosulphate (S_2O_3)	2·20	2·24	2·31	2·25	17·31%
2	Sulphate (SO_4)	9·26	9·30	9·24	9·26	83·16
						100·47
	Temperature = 70°.					
1	Thiosulphate (S_2O_3)	2·31	2·32	2·30	2·31	17·71
2	Sulphate (SO_4)	9·28	9·22	9·23	9·24	83·03
						100·74

Sulphate and thiosulphate represent 100·74% of the lead chromate thus accounting for the whole oxidising power of $PbCrO_4$ and sulphur should be entirely absent. Careful investigation, however, showed the presence of considerable amounts of sulphur. This may be attributed

to the oxidation of hydrogen sulphide by oxygen dissolved in water (*vide* p. 510) and that taken up from the surrounding air during the processes of filtration.

The free sulphur in the 'slow' reaction appears quantitatively as sulphate in the reaction accelerated by the higher temperature.

The Action of Hydrogen Sulphide on Silver Chromate.

Silver chromate was prepared in two varieties (*i*) red, by precipitation of a soluble silver salt with a chromate, and (*ii*) green, by dissolving the red variety in aqueous ammonia and reprecipitating by boiling the solution.

On treating a suspension of 1 g. of pure (red or green) silver chromate in water with about 500 c.c. of H_2S-water, a greenish black substance was ultimately obtained.

The filtrate and washings contained no compound of interest; the precipitate consisted of silver sulphide, chromium sulphate, thiosulphate, sulphite and hydroxide, free sulphur and unattacked silver chromate.

The reaction was conducted in an apparatus in which the particles of silver chromate were ground between the stopper and neck of an inverted wide mouthed bottle from which the bottom had been cut, the stopper being fixed to the base inside a glass dish. The reaction was allowed to proceed in the bottle (which now presented the shape of a beaker with a grinding collar at the base) and, from time to time, it was carefully eased in its seating and rotated with gentle pressure to allow a small quantity of the suspension of partially attacked particles to pass out between the stopper and rotating neck which formed the grinding interface. The fresh surface thus presented was allowed to come in contact with more hydrogen sulphide in the outer vessel. After about two hours' grinding, the filtered residue contained no silver chromate, showing that the reaction was complete.

The products obtained as described for lead chromate were the same as those found in the "bottle" method which was used in all silver chromate work.

Sulphite, thiosulphate and sulphate occur co-ordinated either wholly or in part in a mixture of complex chromium compounds. Evidence on this point was obtained by extraction of the final precipitate with 5% hydrochloric acid. The remaining precipitate contained sulphite, thiosulphate and sulphate. On extraction with 10% HCl, however, the results were negative.

The appearance of sulphite in the final precipitate is of great importance.

Method of analysis.—The precipitate was extracted with 0·3*N* KOH and the filtrate and washings made up to a known volume. A few c.c. of glycerol were added to the extract to stabilise the sulphite against atmospheric oxidation (S. L. Bigelow, *Z. physikal. Chem.*, 1898, **26**, 493). A colourless liquid was obtained in which sulphate, thiosulphate and sulphite were estimated, protecting the sulphite from iodine by the addition of formalin.

The results of these estimations are given in Table VI, values being calculated in a similar manner to those for lead using

48 g. S
36 g. (SO_4)
42 g. (S_2O_3)
and 40 g. (SO_3)
} 331·76 g. Ag_2CrO_4

TABLE VI.

Final greenish-black precipitate.

Values are shown for 100 g. of Ag_2CrO_4 attacked.

Expt.	1 g.	2 g.	3 g.	4 g.	5 g.
1. Sulphite (SO_3)	1·909	1·853	1·803	1·886	1·862
In terms of 100 g. of silver chromate ...					15·44%
2. Thiosulphate (S_2O_3)	4·724	4·724	4·724	4·721	4·724
In terms of 100 g. of silver chromate ...					37·32%
3. Sulphate (SO_4)	3·98	3·87	3·87	3·90	3·905
In terms of 100 g. silver chromate ...					35·98%
4. Sulphur (S)	3·13	3·75	2·90		1·65 (theory)
In terms of 100 g. of silver chromate ...					11·26 (by difference)
5. Chromic oxide (Cr_2O_3)	22·86	22·86	22·89	22·84	22·86
In terms of 100 g. of silver chromate ...					99·78%

The high values of sulphur are again attributable to the oxidation of hydrogen sulphide by atmospheric oxygen and that dissolved in water.

The table below gives the amounts of lead and silver chromates, accounted for by the different sulphur-acid products.

TABLE VII.

Values are shown for 100 g.

	Sulphate.	Thiosulphate.	Sulphite.
In terms of $PbCrO_4$	76·81	18·01	—
In terms of Ag_2CrO_4	35·69	37·32	15·44

In the case of silver chromate, the values for sulphate diminish while thiosulphate increases and sulphite makes its appearance. From this it appears that sulphite and not thiosulphate, is the precursor of sulphate. Hence the authors favour the direct oxidation of sulphoxylic acid as the method of formation of sulphate.

This investigation will be completed in the publication of a further report at an early date when the conclusions from the series of five papers will be summarised.

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Magneto-optical Rotation of Uranyl Salts.

By S. S. Bhatnagar, P. L Kapur and N. R. Verma.

Magneto-optical rotation, both by sign and magnitude, can furnish considerable information with regard to the structure of substances and can supplement the conclusions arrived at by other physico-chemical methods. The usefulness of this method with respect to structural problems has been fully established by Perkin (*J. Chem. Soc.*, 1884, **45**, 421 ; 1885, **47**, 240; *cf.* also Bhatnagar and Mathur, " Physical Principles and Applications of Magneto-Chemistry," Macmillan & Co., London, 1935) and others in the case of organic compounds but its application to inorganic compounds has not been fully explored. The authors' purpose is to undertake a systematic study of ions in different valency states and in the present paper they have studied some of the uranyl salts. The salts of uranium are of a particular interest, because in the case of this element, like that of iron, palladium and platinum, the incomplete shell is the inner *d*-shell with a room for 10 more electrons according to the Pauli exclusion principle. Whereas in the case of iron salts, there is a general agreement between the theoretical and experimental magnetic moments (Bhatnagar and Mathur, *loc. cit.*). This does not seem to be the case with the compounds of uranium. This deviation has been attributed to the complex formation in the aqueous solution, particularly in the case of uranium ions of lower valency state. Lawrence (*J. Amer. Chem. Soc.*, 1934, **56**, 776), has for example, shown that with varying hydrogen ion concentration of the solution, the magnetic susceptibility varies considerably. We have for this reason selected for the present only the uranyl salts for investigation, for in addition to being in the maximum valency state, the uranyl ion exhibits paramagnetism independent of temperature. This type of anomalous paramagnetism is associated with zero Bohr magneton number in such atomic group formations.

Experimental.

Three uranyl salts namely uranyl nitrate, chloride and sulphate were obtained and purified in the laboratory by repeated crystallisations from water. The three salts were further analysed for uranium

and acid radical content. The absence of paramagnetic impurities like manganese, molybdenum and iron, as well as of the uranium salts in lower valency state, was made sure of by standard methods (Noyes and Brans, "Qualitative Analysis for the Rare Elements", Macmillan and Co., New York, 1927; Treadwell and Hall, "Analytical Chemistry", John Wiley and Sons). As a further check the magnetic susceptibilities of the sulphate and nitrate were determined by a Curie-Wilson balance and compared against the standard values given in literature.

The magneto-optical rotations of these salts were determined by the method employed by Bhatnagar and Kapur (*J. Indian Chem. Soc.*, 1934, **11**, 767) and the values of molecular rotations (M) were calculated by the formula,

$$M = \frac{D_2}{D_1}\left[\frac{\mu W_{H_2O} + W_s}{\rho . W_{H_2O}}\right] - \mu \times m$$

where D_2 denotes the rotation of the solution; D_1, the rotation of water; μ, the ratio of the number of molecules of water to one molecule of the solute; ρ, the density of solution; W_{H_2O}, the molecular weight of water; W_s is the molecular weight of solute; m, the molecular rotation of water taken as unity.

After each determination the quantity of the particular salt in the solution was found by analysing a known volume of the solution for the uranium content by the oxide method (Scott, "Standard Methods of Chemical Analysis," D. Von Nostrand and Co., Vol. I) and the quantity of the anhydrous salt was calculated from this. The density of each of the solution was also determined by a 10 c.c. specific gravity bottle. The results obtained are shown in the following tables.

TABLE I.

Uranyl nitrate.

$W = 394{\cdot}17$. $W_{H_2O} = 14$.

No.	Vol.	Density.	Weight of soln.	Weight of solvent.	Weight of solute.	Mols of solvent / Mols of solute	D_2/D_1.	M.
5c	45 c.c.	1·114	50·12g.	43·8839g.	6·2361	154·1	7·82/8·33	−5·70
5d	45	1·075	48·38	44·2226	4·1574	232·8	7·97/8·33	−6·0
5e	45	1·052	47·35	44·5784	2·7716	352·1	8·13/8·33	−5·96
6a	50	1·237	61·85	47·8250	14·0250	74·66	7·29/8·28	−5·35
6b	45	1·157	52·06	43·6450	8·415	113·6	7·60/8·28	−6·1

TABLE II.

Uranyl chloride.

$W_s = 341{\cdot}09$. $W_{H_2O} = 18$.

No.	Vol.	Density.	Weight of soln.	Weight of solvent.	Weight of solute.	Mols of solvent / Mols of solute	D_2/D_1.	M.
2*a*	50	1·175	58·75g.	48·575g.	10·175g.	90·4	8·37/8·55	0·65
2*b*	45	1·116	50·22	44·115	6·105	137·0	8·47/8·55	1·50
3*b*	45	1·094	49·23	43·990	5·2335	159·3	8·45/8·55	1·50

TABLE III.

Uranyl sulphate.

$W_s = 366{\cdot}17$. $W_{H_2O} = 18$

No.	Vol.	Density.	Weight of soln.	Weight of solvent.	Weight of solute.	Mols of solvent / Mols of solute	D_2/D_1.	M.
1*a*	50 c. c.	1·151	57·55 g.	49·505 g.	8·045 g.	125·1	7·935/8·56	−8·0
1*b*	45	1·102	49·59	44·763	4·827	188·7	8·112/8·56	−9·0
1*d*	60	1·026	61·56	59·951	1·609	758·0	8·46/8·56	−8·4

DISCUSSION.

The molecular rotation value due to the uranyl ion can be calculated by subtracting the rotation due to other ions from that of the pure salt. From Anderson and Asmussen's data (*J. Phys. Chem.*, 1932, **36**, 2827) on a series of inorganic compounds the following values for rotations of different substances and ions have been obtained: Cl', 4·43; $(NH_4)_2SO_4$, 4·99 ; $(NH_4)'$, 1·00.

By subtracting the molecular rotation on account of NH_4' from that of the sulphate, the rotation of the sulphate radical comes out to be 2·99. Similarly the rotation of the nitrate group as calculated from Humburg's data (*Z. Physik*, 1893, **12**, 401) work out to be 1·150.

In Table IV are given the rotation values due to the uranyl ion.

TABLE IV.

Salt.	No.	M.	M_{anion}	$M_{(UO_2)^{..}}$
Uranyl nitrate	5c	−5·70	2×1·150=2·30	−5·7−2·3=−8·0
	5d	−6·00	,,	−6·0−2·3=−8·3
	5e	−5·96	,,	−5·95−2·3=−8·25
	6a	−5·93	,,	−5·93−2·3=−8·23
	6b	−6·1	,,	−6·1−2·3=−8·4
Uranyl chloride	2a	0·65	2×4·43=8·86	0·65−8·86=−8·21
	2b	1·50	,,	1·50−8·86=−7·36
	3b	1·50	,,	1·50−8·83=−7·36
Uranyl sulphate	1a	−8·0	2·99	−8·0−2·99=−10·99
	1b	−9·0	2·99	−9·0−2·99=−11·99
	1d	−8·4	2·99	−8·4−2·99=−11·39

It may be seen that value for rotation of UO_2 has in each case a negative sign and in the case of individual salts is fairly constant over a wide range of concentration. One more fact which is quite significant is that the molecular rotation value due to uranyl radical has nearly the same value in the case of the nitrate and the chloride but the case of the sulphate shows a much different rotation. This difference in molecular magnetic rotation value of UO_2 in the case of sulphate may be due to the existence of some complex formation. On analysing completely all the three salts the composition of the chloride and the nitrate proved to be UO_2Cl_2 and $UO_2(NO_3)_2$, but that of the sulphate worked out to be $2UO_2 \cdot SO_4 \cdot H_2SO_4 \cdot 5H_2O$ corresponding to the formula of Wyrobouff (*Bull. Soc. franc., min.*, 1909, **32**, 340). Our observation of the Faraday-effect, therefore, show that the anomaly may be due to the sulphuric acid molecule entering into complex formation with the uranyl ion thus affecting the value of molecular rotation.

The magnetic susceptibiiity of the uranyl ion as a sulphate has been determined in aqueous solutions (Lawrence, *loc. cit.*) as well in the solid state (Freed and Kasper, *J. Amer. Chem. Soc.*, 1930, **52**, 4671). The ion has been found to be slightly paramagnetic though the susceptibility is independent of temperature.

It is significant to note that certain compounds which exhibit anomalous paramagnetism with respect to temperature also show that Faraday-effect independent of temperature, for example (Mlle) Collet (*Compt. rend.*, 1926 **183,** 1031) observed that the paramagnetic susceptibility of $KMnO_4$ and $K_2Cr_2O_7$ does not show any variation with temperature. Also Pillai (*Indian J. Phys.*, 1932, **6**, 573) showed that Faraday-effect in these compounds is as well independent of temperature. One may, therefore, expect the rotation of the uranyl salts also not to be affected by temperature since their susceptibility does not show any variation under the conditions. This, however, is not a general rule, for there are substances like manganese chloride and cobalt nitrate which obey Weiss law but show a constant magneto-optical rotation over the range of temparature investigated. Work, however, on the effect of temperature on the magneto-optical rotation of uranyl salts is in progress. We are also studying the effect of addition of free acids of the magneto-optical rotation of these salts.

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The Anomalous Rotatory Dispersion of *l*-β Pinene. Part I.

BY R. PADMANABHAN AND S. K. KULKARNI JATKAR.

In a previous work (Padmanabhan and Jatkar, *J. Amer. Chem. Soc.*, 1935, **56**, 334) on the rotatory dispersion of seven isomeric hydrocarbons of the formula $C_{10}H_{16}$, the interesting observation that the optical rotatory power of *d*-sabinene passes through a maximum at about λ 3300 Å was made. Since *d*-sabinene and *l*-β-pinene are the only substances having anomalous rotatory dispersion known up till now among the optically active hydrocarbons, we felt that further work was desirable in order to throw light upon the origin of the peculiar optical behaviour of these compounds.

The optical rotatory power of *l*-β-pinene is negative in the visible region of the spectrum, the magnitude changing but slightly with wave-length, becomes zero at about λ 3700 Å and attains high positive values on the shorter wave-length side. This anomalous behaviour was first noticed by Darmois (*Ann. chim. phys.*, 1911, **22**, 495) and although both he and quite recently Servant (*Compt. rend.*,

1932, **194**, 368) have measured the rotatory dispersion in the visible and in the ultraviolet, they have not attempted to explain the origin of the anomaly. It is not evidently due to the Cotton-effect, since an examination of the substance in alcoholic solution by the Hartley-Baly method shows the absence of any absorption in the anomalous region.

If we compare the formula of sabinene and β-pinene, it will be observed that both the compounds are characterised by the presence of a semicyclic double bond adjacent to an asymmetric carbon atom. According to Lowry and Walker (*Nature*, 1924, **115**, 365) chromophoric groups when coupled sufficiently closely to an asymmetric complex can exhibit an induced asymmetry, as a result of which they may themselves become optically active. The semicyclic double bond has also been known to have a powerful influence on the refractive dispersion (Wallach, *Annalen*, 1908, **360**, 34; Auwers and Ellinger, *ibid.*, 1912, **387**, 200). Since induced asymmetry need not always lead to an optical rotation of the same sign as that of the fixed asymmetric groups by which it is controlled, it appeared as if the proximity of the double bond to an asymmetric carbon atom were responsible for the anomaly. However camphene (Padmanabhan and Jatkar *loc. cit.*) which also possesses the same characteristics does not show any signs of anomalous rotatory dispersion up to 3100Å.

It seemed probable that the presence of a *dextro*-rotatory second component having a different rotatory dispersive power and which is separable from β-pinene only with great difficulty might give rise, by superposition of the two rotatory dispersions, to this anomaly in the region of transparency. Nopinene (β-pinene) is one of the most commonly occurring among the terpenes, being almost always associated with α-pinene in many turpentine oils and has been isolated by several workers (Dupont, *Ann. chim. phys.*, 1924, *i*, **10**, 184; Austerweil, *Chim. Industrie, special no.*, 1926, 603). Nevertheless the simultaneous occurrence of closely related substances and the tendency so common among the terpenes to distil together in spite of a difference in boiling point of several degrees, made it seem probable that even if nopinene were really heterogenous it might have escaped notice by previous workers. Although this expectation has not been realised, our work makes it clear that elaborate purification—much more than what is usually attempted in most of the work on terpenes—is necessary in order to free β-pinene from associated impurities.

Purification and Darmois Diagram.

Unfortunately no crystalline derivative of nopinene is known from which the parent hydrocarbon could be regenerated so that only physical methods like fractional distillation are available for purification. A commercially available pure sample of nopinene was, therefore, fractionally distilled in a very efficient rectifying column. The practically constant boiling point (62°/21 mm.) of the starting material would lead one to the belief that it was homogenous but by the maintenance of a suitable reflux ratio and by the systematic addition of each fraction when nearly half the previous fraction had distilled over, and by carrying out the distillation in an atmosphere of dry carbon dioxide to prevent the formation of oxidation products, it was found that after nine redistillations there was a gradual transition from a *laevo*-rotatory substance in the first fraction to a *dextro*-rotatory substance of higher rotatory dispersive power in the last, both having normal dispersion in the visible spectrum (normal only in the sense that rotation increases with decreasing wave-length). This appears to point to the conclusion that the various fractions are but mixtures in varying proportion of these two compunds and that the anomalous R. D. of the middle fractions is due to the superposition of the rotatory dispersions of these substances. The heterogenous nature of nopinene is thus rendered plausible by these results but it was noticed that they could also be explained if we postulate the occurrence along with nopinene in the turpentine oil from which it was isolated, a *laevo*-rotatory constituent of lower boiling point and a less volatile *dextro*-rotatory constituent. In order to decide between these two possible alternatives, the rotations of the various fractions for the wave-lengths 5780Å and 4358Å were represented on a Darmois diagram (Darmois, Thesis de Doctorate, Paris, 1910) which permits one to recognise whether there are two or more than two optically active substances in a mixture. If we consider a mixture of two substances whose specific rotatory powers are (α_1) and (α_2) while x and $1-x$ are the proportion in which they occur, the specific rotatory power of the mixture $[\alpha]=x\,[\alpha_1]+[1-x]\,[\alpha_2]$ from this one gets the relation,

$$\frac{1-x}{x} = \frac{[\alpha_1]-[\alpha]}{[\alpha]-[\alpha_2]}.$$

In Fig. 1 if OA_1, OB_1, and OC_1, represent for a wave-length, λ_1, the specific rotatory powers of the two pure substances and the

mixture respectively, it follows from the above relation that the ratio C_1A/C_1B is independent of the wave-length. Hence if A_2, B_2 and C_2 are the corresponding points for another wave-length λ_2, A_1A_2, B_1B_2 and C_1C_2 must be concurrent. Conversely, if a mixture is resolved into fractions whose dispersions could be represented by such a diagram it should contain only two components.

FIG. 1.

Darmois diagram.

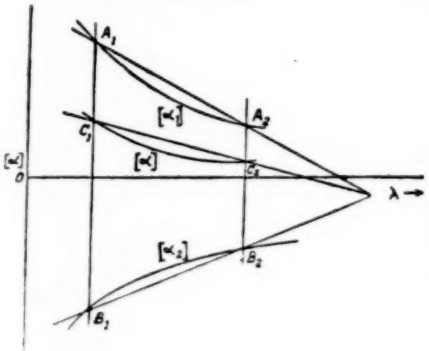
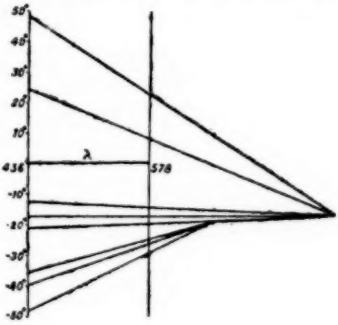


FIG. 2.

Darmois diagram of β-pinene fractions.



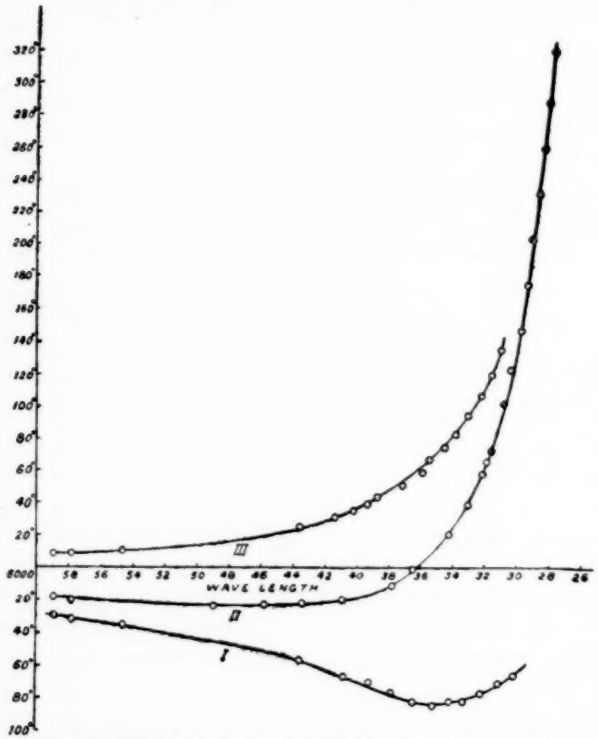
Applying this to the case of β-pinene (Fig. 2), it is evident from the figure that there are three substances involved, the head and the tail fractions representing two component mixtures of a *laevo* and a *dextro*-rotating compound respectively with β-pinene isolated in a practically pure form in the middle fractions and having anomalous rotatory dispersion. The origin of the anomaly cannot, therefore, be explained away by attributing it to the presence of an impurity.

Raman spectra.—Further support for this conclusion is furnished by a study of the Raman-effect of the head, middle and tail fractions. The data are tabulated in Table I. It can be observed that a number of frequencies occuring as strong lines in the head and tail fractions does not occur even as faint lines in the middle fraction and *vice versa*. This cannot be explained if we assume that the middle fraction is a mixture and on purification is splitting up into its components. The citrus like odour of the last fraction and the previous observation of Dupont and Barrand (*Bull. Inst. Pin.*, 1928, **45**, 76) that β-pinene from *Pinus Maritima* is associated with limonene and dipentene led us to compare the Raman spectra of the two substances with that of

the last fraction but no resemblance whatsoever was found. The Raman spectra of pure β-pinene will be discussed in a subsequent communication. It is not however out of place to point out the fact that the long shifts ignored by Dupont are very characteristic of the terpenes.

FIG. 3.

Rotatory dispersion of β-pinene fractions.



Curves I—III refer to head, middle and tail fractions respectively.

Rotatory dispersion of β-pinene.—The rotatory dispersions of the three fractions were determined by an improved method to be published shortly. The results are given in Table II. As seen from Fig. 3., the head fraction is contaminated with an appreciable percentage of β-pinene, the anomalous rotatory dispersion of which makes itself felt in the region of shorter wave-lengths. The high rotatory dispersive power of the tail fraction can likewise be attributed to the same cause. The rotatory dispersion curve of the middle fraction which is

taken as representing that of a fairly pure sample of β-pinene does not differ appreciably from those given by the two previous workers, Darmois and Servant in the longer wave-lengths, but the second anomaly reported by the latter at λ 2830 Å (*loc. cit.*) has not been confirmed by us although our measurements extend up to 2780Å. We are attempting to extend the measurements further into the ultraviolet by using a hydrogen discharge tube as the light source.

Experimental.

500 G. of a sample of β-pinene (Schuchardt) of the following rotation in the visible $\alpha_{589} = -16{\cdot}8$, $\alpha_{578} = -17{\cdot}1$, $\alpha_{546} = 18{\cdot}2$, $\alpha_{436} = 18{\cdot}8$, were dried over anhydrous magnesium sulphate and distilled over sodium under reduced pressure using a Widner-Schenck fractionating column. Eight fractions were obtained having the following rotations :

Fraction ...	1	2	3	4	5	6	7	8
α_{578} ...	−21·7	−20·6	−20·5	−19·6	−19·2	−17·8	−15·9	−6·6

The temperature was constant (62°/21 mm.) practically throughout the distillation. These were then redistilled in order, a fraction being added when nearly half the previous fraction had distilled over. After four such redistillations the following values were obtained for the consecutive fractions.

Fraction ...	33	34	35	36	37	38
α_{578} ...	−26·7	−25·0	−24·6	−21·5	−21·0	−20·7
Fraction ...	39	40	41	42	43	44
α_{578} ...	−20·0	−19·3	−18·7	−17·6	−12·5	−1·9

The separation though gradual is quite perceptible. The purification was, therefore, continued, and to have a better insight into the progress of the separation, the rotation for the three wave-lengths 5780, 5461, 4358 were measured. After three redistillations, the values were as follows.

Table I.

Fraction No.	α_{578}.	α_{546}.	α_{436}.	Fraction No.	α_{578}.	α_{546}.	α_{436}.
84	−29·3	−32·5	−48·0	92	−19·1	−20·2	−19·8
85	−26·2	−28·9	−39·6	93	−18·8	−20·0	−19·1
86	−24·7	−26·9	−35·1	94	−18·7	−19·7	−18·8
87	−23·7	−25·8	−32·4	95	−18·3	−19·4	−18·4
88	−23·0	−25·0	−30·7	96	−17·5	−18·5	−17·1
89	−21·9	−23·7	−27·5	97	−14·5	−15·2	−12·5
90	−20·3	−21·7	−23·1	98	+ 8·3	+ 9·7	+24·9
91	−19·4	−20·6	−20·6	99	+22·3	+25·9	+48·4.

Further purification was not attempted since the fractions 92-95 had nearly equal rotations and dispersions. The Darmois diagram of these fractions are represented in Fig. 2.

Raman Spectra.

The Raman spectra were obtained with a Fuess spectrograph having a dispersion 28Å/mm. Different exposures varying from 8-24 hours were given.

The wave-lengths of the Raman lines along with the shift in wave-numbers were measured. In order to bring out the differences in light scattering between the fractions, the shifts alone are tabulated separately (Table II).

TABLE II.

Comparative table showing the Raman spectra data.

Head fraction.	β-Pinene Middle fraction.	Tail fraction.	Dupont β-pinene.	Bonino *l*-Limonene.
301 (3)	296 (2b)			
335 (3)	327 (2b)	328 (2)		316 (½)
	385 (1b)	391 (2)	391 (1b)	
		418 (2)		435 (1)
	468 (2)		480 (2)	
				525 (1)
554 (4)	552 (3)	551 (4)		552 (1)
641 (3)	639 (5)	640 (4)	648 (5)	643 (0)
662 (3)		657 (4)		
	713 (1)			
761 (2)	761 (2)			765 (3)
			778 (2b)	
	814 (2)			802 (2)
	848 (4)		850 (5)	
	872 (4)	867 (1)	879 (5)	890 (1)
	923 (2)			916 (1)
948 (3)	949 (2)		942 (4b)	950 (1)
	1010 (3)			
	1045 (2)		1048 (3)	
	1096 (3)		1091 (1b)	
	1126 } (5b)		1134 (3)	
	1186 }			1168 (1)
	1214 (5b)		1224 (4b)	
1256 (3)	1254 (3)		1251 (2)	
	1298 }			
	} (2)	1308 (2)		1378 (2)
	1411 }			
1442 (3)	1432 (2b)	1428 (3)	1430 (8bb)	1446 (5)
		1616 (3)		
	1638 (5)	1634 (3)	1641 (10)	
1651 (3)		1668 (3)		1658 (3)
				1680 (3)
	2869 (1)			2860 (4)
2921 (3b)	2933 (2b)	2915 (3b)		2923 (4)
2985 (3b)	2987 (2)	2971 (3)		2973 (1)
3047 (3)		3047 (5)		
	3074 (4)			3082 (2)
3125 (3)		3126 (3)		
	3153 (4)			3156 (0)

TABLE III.

Rotatory dispersion of β-pinene.

Head fraction.		Middle fraction.				Tail fraction.	
Rotation.	λ.	Rotation.	λ.	Rotation.	λ.	Rotation.	λ.
−29·77	5893	−19·53	5893	33·5	3348	7·8	5893
−31·88	5780	−20·04	5780	38·9	3297	8·2	5780
−35·60	5461	−21·38	5461	46·6	3275	10·1	5461
−56·80	4358	−22·11	4358	54·4	3220	25·5	4358
−66·4	4078	−23·2	5100	57·9	3208	27·2	4297
−70·0	3920	−23·6	4893	65·6	3186	31·2	4134
−76·8	3775	−23·2	4735	72·5	3161	35·2	4017
−82·2	3638	−23·1	4584	102·0	3082	39·2	3932
−84·4	3525	−22·9	4147	123·2	3036	43·2	3866
−82·2	3408	−22·2	4312	147·2	2980	51·2	3709
−81·5	3325	−19·0	4090	174·8	2940	59·2	3580
−77·2	3214	−17·7	4010	204·0	2906	67·2	3540
−70·8	3103	−11·1	3781	231·6	2871	75·2	3452
−66·0	3012	− 0·8	3644	260·0	2837	83·2	3378
		10·5	3535	288·4	2806	95·2	3305
		15·1	3472	319·6	2782	107·2	3223
		20·5	3420			119·2	3157
						135·2	3099

SUMMARY.

1. The rotatory dispersions of a pure sample of β-pinene till λ2780Å and of the head and tail fractions have been measured by a modification of the usual photographic method. This has been found necessary on account of the smallness of the rotatory dispersion in the visible and near ultraviolet regions of the spectrum.

2. A prolonged purification by fractional distillations of a sample of the substance seems to indicate that the anomaly at 2800Å reported by Servant is due to a closely associated impurity,

which is separable from β-pinene only with great difficulty. A Darmois diagram of the various fractions shows, however, that anomalous rotatory dispersion in the near ultraviolet still remains a characteristic of β-pinene. This conclusion is supported by Raman effect data of the various fractions obained.

3. The anomalous rotatory dispersion of β-pinene is not due to Cotton-effect because there is no evidence of any absorption in the region of the anomaly. It must, therefore, be due to a superposition effect caused by a second rotation of opposite sign and having a different dispersion.

4. This second rotation cannot be attributed to the 'induced dissymmetry' of the semicyclic double bond because camphene which is also similarly constituted has been shown in a previous work to possess normal dispersion.

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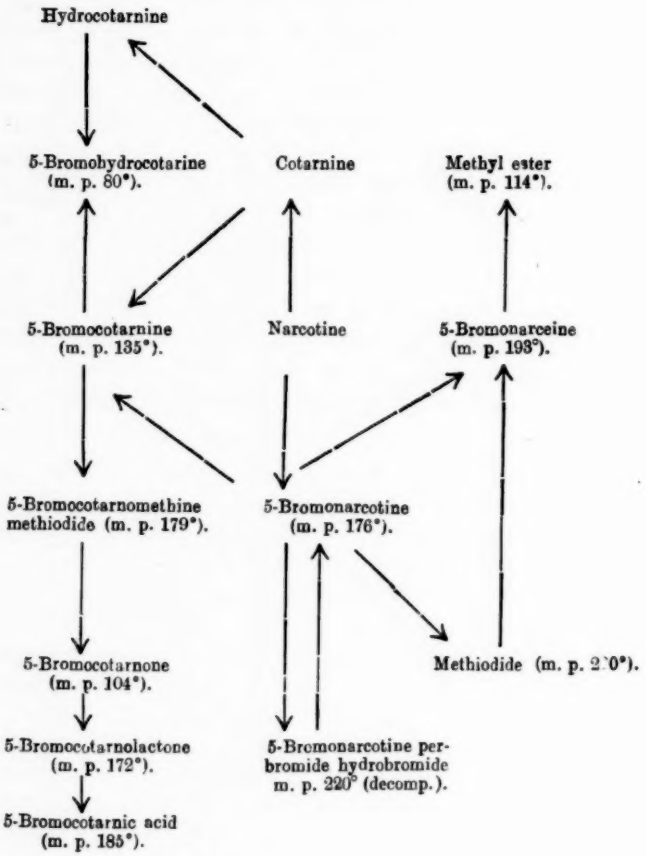
Studies in the Cotarnine Series. Part IV. 5-Bromonarcotine, 5-Bromocotarnine, 5-Bromohydrocotarnine and 5-Bromonarceine and their Derivatives.

BY B. B. DEY AND T. K. SRINIVASAN.

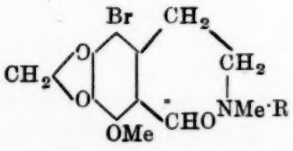
The only references to literature about bromocotarnine and bromohydrocotarnine are to be found in two papers by Wright (*J. Chem. Soc.*, 1877, **32**, 525) and by Heimann (Dissertation, Marburg, 1892, p. 15 ; also Small, "Chemistry of the Opium Alkaloids," 1932, pp. 68, 70, 98). Bromonarcotine and bromonarceine do not appear to have been prepared before.

Wright examined in detail the action of bromine water on a solution of hydrocotarnine in hydrobromic acid. He obtained a bromohydrocotarnine (m.p. 76°), and a perbromide of the latter which was supposed to decompose on standing in the presence of water into bromocotarnine and hydrobromic acid. As it seemed very remarkable that hydrocotarnine could be so easily oxidised to cotarnine by simple treatment with bromine water, we repeated this work with care, but although we readily obtained bromohydrocotarnine and the perbromide in a pure condition, we have been unable te confirm Wright's observation that bromocotarnine was formed in this reaction. The low melting point recorded by Wright (100° instead of 135°) also indicates the bromocotarnine, if obtained at all, having been very impure. Heimann (*loc. cit.*) prepared bromocotarnine by the action of bromine water on a solution of cotarnine hydrochloride, the precipitated perbromide being reduced with H_2S.

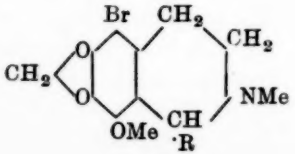
The bromination of narcotine in cold acid solution proceeds smoothly and leads to the formation of almost the theoretical quantity of 5-bromonarcotine perbromide hydrobromide which is fairly stable and crystallises from alcohol in light yellow needles, (m.p. 220° decomp.). The reduction of the latter in the usual way gives 5-bromonarcotine crystallising in colourless needles (m. p. 176°). Oxidation of the latter with nitric acid gave almost a theoretical yield of 5-bromocotarnine (yellowish white needles, m. p. 135°, identical with the product obtained from cotarnine by direct bromination) and opianic acid. Similarly, 5-bromonarceine crystallising in silky needles (m. p. 193°) was readily obtained from the bromonarcotine by steaming a mixture of the latter with methyl-*p*-toluene sulphonate and sodium hydroxide (Rodionov, *Bull. Soc. chim.*, 1926, **39**, 305). The position of the bromine atom in all these derivatives has been settled by the conversion of 5-bromocotarnine through exhaustive methylation into 5-bromocotarnone and oxidation of the latter into 5-bromocotarnolactone, and finally into 5-bromocotarnic acid. A further argument in support of this position being assigned to the bromine atom in these derivatives is derived from the observation that neither 5-bromocotarnine nor 5-bromonarcotine condenses with formaldehyde which is known to attack only the 5 position in these bases, when free. Our results are summarised in the scheme given on the next page.



The formulæ of most of the compounds described in this paper may be referred to either of the two following types:



(I)



(II)

Experimental.

5-Bromonarcotine.—Finely powdered narcotine (5 g.) was dissolved in 20 c. c. of water containing 2 c. c. of 48% HBr, the solution cooled in ice and saturated bromine water added with constant stirring until the yellowish white precipitate which redissolved on shaking, became permanent. The turbid solution was then treated with sulphuretted hydrogen, the solution filtered from any precipitated sulphur and the clear solution basified with ammonia. The bromonarcotine was filtered after an hour, washed with water and dried on a porous plate and crystallised from 90% alcohol as colourless needles, m. p. 176°, yield 5·5 g. [Found (in sample dried at 100°): C, 53·51 ; H, 4·53 ; Br, 15·84. $C_{22}H_{22}O_7N{\cdot}Br$ requires C, 53·65 ; H, 4·47 ; Br, 16·26 per cent]. 1·13 G. of the substance in 25 c. c. of chloroform solution gave in a 2 dcm. tube a rotation of −4·29°; $[\alpha]_D^{30°} = -95°$. In dilute mineral acids the substance goes into solution, but not immediately. The base is difficultly soluble in alcohol but dissolves easily in acetone and chloroform. It imparts a carmine-red colour to concentrated sulphuric acid, whereas narcotine gives only a yellow colour. The hydrochloride and hydrobromide are sparingly soluble and separate from solutions of the base in moderately strong acids.

The *hydrochloride* forms a white crystalline powder, m. p. 120°. [Found (on heating at 110° over P_2O_5 at 5 mm.): Cl(HCl), 6·61 ; H_2O, 3·06. $C_{22}H_{22}O_7N\,Br$, HCl, H_2O requires Cl(HCl), 6·49 ; H_2O, 3·29 per cent].

The *hydrobromide* formed a similar powder melting at 168°. [Found: Br(HBr), 13·67 ; H_2O, 3·33. $C_{22}H_{22}O_7NBr$, HBr, H_2O requires Br(HBr), 13·53 ; H_2O, 3·04 per cent].

The *perbromide hydrobromide.*—Narcotine (0·5 g.) was dissolved in dilute HBr and saturated bromine water slowly added with continuous stirring until precipitation was complete. The precipitate was collected at once, washed rapidly with cold water, dried and crystallised from hot 90 % alcohol as fine yellow needles darkening at 210° and melting at 220° (decomp.); the pure product weighed 0·7 g. On passing H_2S through a suspension of the perbromide in water and basifying the clear solution with ammonia, 5-bromonarcotine, m. p. 176°, was recovered completely. Three out of the 4 bromine atoms in the perbromide were estimated by warming the substance

with dilute caustic soda, acidifying with nitric acid and precipitating the bromide with silver nitrate. [Found: Br, 33·05. $C_{22}H_{22}O_7NBr_3$, HBr requires (for 3 atoms of Br,) Br, 32·74 per cent].

The *platinichloride* was thrown down as a pale yellow granular powder. [Found: Pt, 13·7. $(C_{22}H_{22}O_7NBr, HCl)_2$ $PtCl_4$ requires Pt, 14·0 per cent].

The *picrate* crystallises from alcohol in yellow rectangular plates, m. p. 197°. (Found: C, 46·2 ; H, 4·01. $C_{28}H_{25}O_{14}N_4Br$ requires C, 46·6 ; H, 3·46 per cent).

The *methiodide*, prepared by heating the components in a pressure bottle at 100° for 3 hours and crystallising the dark brown mass twice from hot dilute alcohol (charcoal), formed stout colourless needles, m. p. 220°. [Found (in a sample dried at 110° in vacuum): C, 43·39 ; H, 4·45. $C_{22}H_{25}O_7NBrI$ requires C, 43·53 ; H, 3·94 per cent].

5-Bromocotarnine. (*a*) *By oxidation of bromonarcotine.*—Nitric acid (*d* 1·4, 20 c. c.) was diluted with water (50 c. c.), the acid warmed to 49° and finely powdered bromonarcotine (10 g.) added in small quantities with continuous stirring, the whole process requiring about an hour. The clear yellow solution was transferred to a stoppered bottle, shaken mechanically for half an hour and then left overnight in a large vacuum jar containing water at about 50°. The filtered solution was cooled in ice, a strong solution of caustic soda added gradually with stirring and the precipitated bromocotarnine washed and dried on a plate; yellowish white powder, m. p. 129-30°, weighing nearly 6 g. One crystallisation from alcohol gave pure white needles, m. p. 135°. It is sparingly soluble in cold alcohol but dissolves readily in hot alcohol, acetone and chloroform. [Found (in sample dried in vacuum over KOH): C, 45·0 ; H, 4·41. $C_{12}H_{14}O_4N$ Br requires C, 45·56 ; H, 4·43 per cent]. The *hydrochloride*, obtained by evaporating the acid solution over H_2SO_4 in vacuum, was very soluble in water, m. p. 170° (decomp.).

(*b*) *By bromination of cotarnine.*—Cotarnine (5 g.) dissolved in dilute HBr, was treated with excess of saturated bromine water (400 c. c.) till there was no further precipitation. The orange-red precipitate was filtered, washed and suspended in water and decomposed by H_2S. The precipitate obtained by basifying the clear

solution with caustic soda, crystallised from alcohol in colourless needles, m. p. 135°, yield 3·4 g.

The method of preparing bromocotarnine by oxidation of bromonarcotine is much to be preferred to the latter method both on account of the simplicity of the process and the improved yield of the product.

The *perbromide hydrobromide* was prepared from the orange-red precipitate obtained above by drying and crystallising from hot alcohol as beautiful orange-red needles, m. p. 200° (decomp.). [Found (in material dried in vacuum at room temperature): C, 26·33 ; H, 2·72. $C_{12}H_{12}O_3N\,Br_3$, HBr requires C, 26·71 ; H, 2·41 per cent]. The available bromine in the perbromide was also estimated as follows:— A weighed amount was dissolved in methanol and treated with excess of potassium iodide solution followed by dilute H_2SO_4, the liberated iodine being titrated at once against standard thiosulphate. (Found: available Br, 29·49. $C_{12}H_{12}O_3N\,Br_3$, HBr requires Br, 29·68 per cent).

The *picrate* crystallises from alcohol in yellow needles, m.p. 171°.

The *platinichloride* came down as a pale yellow crystalline powder. [Found: Pt, 19·63. $(C_{12}H_{12}O_3N\,Br,\,HCl)_2\,PtCl_4$ requires Pt, 19·4 per cent].

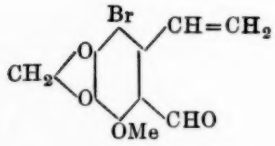
5-Bromocotarnomethine methiodide, prepared by heating the components under pressure in the usual manner, crystallised from hot water in stout straw-yellow needles, m.p. 179°, yield quantitative. (Found: C, 35·22 ; H, 4·05. $C_{14}H_{19}O_4N\,Br\,I$ requires C, 35·59 ; H, 4·02 per cent).

Benzoyl-5-bromocotarnine (I, R=CO·Ph) was prepared by rubbing in a mortar a suspension of bromocotarnine (1 g.) in excess of dilute alkali with benzoyl chloride (10 drops) until the oil solidified completely. Crystallisation from dilute alcohol gave short colourless prisms, m.p. 103°. (Found: C, 53·91 ; H, 4·63. $C_{19}H_{18}O_5NBr$ requires C, 54·28 ; H, 4·28 per cent).

5-Bromocotarnine oxime hydrochloride separated as yellow crystals on warming an alcoholic solution of bromocotarnine with hydroxylamine hydrochloride and sodium acetate and then diluting it with water. Crystallisation from dilute alcohol gave colourless

needles, m.p. 169°. The free *oxime* was obtained by basifying the aqueous solution with ammonia and crystallising it from alcohol as needles, m.p. 138°. (Found: C, 43·32 ; H, 4·21. $C_{12}H_{15}O_4N_2Br$ requires C, 43·50 ; H, 4·53 per cent).

5-Bromocotarnone.



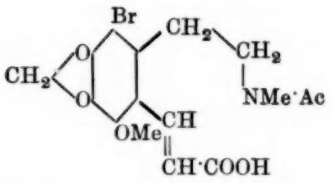
A mixture of the cotarnomethine methiodide (2 g.) and caustic soda (10 %, 20 c.c.) was distilled in steam till the distillate was neutral. A small part of the bromocotarnone volatilised with the steam and condensed in the receiver as white flakes ; the major portion remained in the flask and separated as a dark amorphous mass on cooling. Two crystallisations from very dilute alcohol (charcoal) gave a mass of light colourless needles, m.p. 104°. (Found: C, 46·65 ; H, 3·11. $C_{11}H_9O_4Br$ requires C, 46·31 ; H, 3·15 per cent).

5-Bromocotarnomethylphenyl urea (I, R=CO·NH·Ph).—5-Bromocotarnine (1 g.), suspended in benzene (10 c.c.) was treated with a few drops of phenyl *iso*cyanate. The reaction was vigorous and crystals of the urea derivative separated almost immediately, m.p. 160°. It is insoluble in dilute acids. (Found: C, 53·1 ; H, 4·5; N, 6·1. $C_{19}H_{19}O_5N_2Br$ requires C, 52·42; H, 4·36 ; N, 6·43 per cent).

The *oxime* was prepared in the usual way. It crystallised in flat shining needles, m.p. 168-69°. (Found: N, 9·66. $C_{19}H_{20}O_5N_3Br$ requires N, 9·34 per cent).

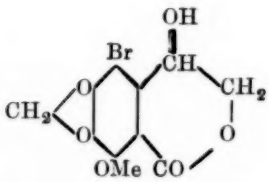
Anhydrobromocotarnino-nitromethane (II, R=CH_2·NO_2).— A warm alcoholic solution of bromocotarnine (1 g.) was mixed with nitromethane (12 drops) and heated just to boiling and allowed to stand. The product separated out on cooling as silky colourless needles which were recrystallised from alcohol, m.p. 148°, yield quantitative. (Found: C, 43·05 ; H, 4·31. $C_{13}H_{15}O_5N_2Br$ requires C, 43·45 ; H, 4·17 per cent). It yields a sparingly soluble hydrochloride crystallising in prisms, m.p. 166°.

N-Acetyl-5-bromocotarnideneacetic acid.



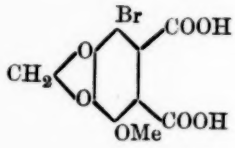
This was prepared by heating bromocotarnine and excess of acetic anhydride to boiling for 10 minutes, diluting it with water and dissolving the precipitate which collected after 24 hours in dilute sodium carbonate and reprecipitating with acid. Crystallisation from dilute alcohol (charcoal) gave colourless prismatic needles, m.p. 211°. (Found: C, 48·51 ; H, 4·61. $C_{16}H_{18}O_6NBr$ requires C, 48·0 ; H, 4·50 per cent). The acid formed a white silver salt. (Found: Ag, 20·88. $C_{16}H_{17}O_6NBrAg$ requires Ag, 21·30 per cent).

5-Bromocotarnolactone.



Bromocotarnone (1 g.) was dissolved in acetone (3 c.c.), a solution of potassium carbonate (1 g. in 5 c.c. of water) added and the solution treated in the cold with powdered potassium permanganate (1·2 g.) added gradually during an hour. The bottle containing the mixture was shaken mechanically for 3 hours and after leaving overnight, the solution was filtered, the acetone removed on the water-bath, and the separating solid, mixed with brown oxides of manganese, was washed with a little sulphurous acid and crystallised from dilute alcohol (charcoal) as colourless crystals having a characteristic appearance of cut diamonds, m.p. 172°. (Found: C, 41·98 ; H, 3·24. $C_{11}H_9O_6Br$ requires C, 41·64; H, 2·83 per cent).

5-Bromocotarnic acid (2-methoxy-3:4-methylenedioxy-5-bromophthalic acid).



5-Bromocotarnolactone (0·5 g.) was dissolved in caustic soda (10%, 10 c.c.) by warming and a solution of potassium permanganate (0·6 g. in 20 c.c. of water) added drop by drop with vigourous shaking. The solution was filtered after an hour, sulphur dioxide passed and the clear, colourless solution was concentrated on the water-bath and left overnight. The crystalline powder which separated out was dissolved in cold sodium carbonate and was reprecipitated on adding acid. Crystallisation from dilute alcohol gave small colourless plates, m.p. 185°, yield 0·15 g. (Found: C, 37·69 ; H, 2·54. $C_{10}H_7O_7Br$ requires C, 37·61 ; H, 2·19 per cent). The *anhydride*, m.p. 225°, was obtained on heating the acid to 200° for a few minutes.

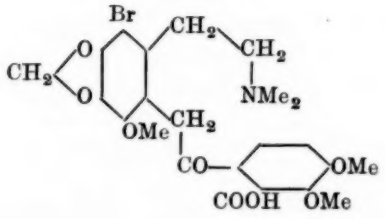
5-Bromohydrocotarnine.—Bromocotarnine (1 g.) was dissolved in *N*-HCl (20 c.c.) and 4% sodium amalgam added in small quantities at a time, the solution being kept acidic throughout the reduction. The clear solution was basified with strong caustic soda, extracted thrice with ether, dried over potassium carbonate and the ether removed on the water-bath. The yellowish oil which was left behind was rubbed with a few drops of HBr and the solid hydrobromide collected and washed with a little cold water ; the free base was liberated with caustic soda and crystallised first from ether and then from a mixture of benzene and petroleum as colourless plates, m.p. 80° (Wright records m.p. 76°), yield 0·6 g. The same product was obtained also in good yield by brominating hydrocotarnine in acid solution by Wright's method.

The *hydrobromide* is sparingly soluble and crystallises from hot water as colourless needles, m.p. 242°. [Found: Br (HBr), 20·99. $C_{12}H_{14}O_3NBr$, HBr requires Br (HBr), 20·90 per cent].

The *perbromide hydrobromide*, prepared in the usual manner, crystallises from alcohol in orange coloured plates, m.p. 166° (decomp.). The available bromine was estimated by the method described before. [Found: Br, 29·34. $C_{12}H_{14}O_3N$ $Br.Br_2HBr$ requires Br (available), 29·57 per cent].

Attempts to obtain bromocotarnine from the above by leaving it in contact with water or by warming a suspension of the substance in water were unsuccessful. In every case reduction of the solution with H_2S in the usual way yielded only the unchanged bromohydrocotarnine.

5-Bromonarceine.



A mixture of 5-bromonarcotine (5 g.) and methyl-*p*-toluene sulphonate (4 g.) was heated on a boiling water-bath for 45 minutes and then for half an hour in a glycerol-bath at 110°-120°. The syrupy liquid was made slightly alkaline with caustic soda and steam passed in for 2 hours. The dark coloured solid which separated out of the solution after 12 hours was collected and purified by dissolving in hot alcohol (charcoal) and adding water till it was permanently turbid. The precipitate was collected after 12 hours and crystallised twice from boiling water which deposited rosettes of soft colourless needles, m.p. 193°, yield 2·7 g. It dissolves readily in alcohol and most of the common organic solvents; it is sparingly soluble in water. It forms sparingly soluble salts with the mineral acids. The material did not lose weight on drying at 100° in vacuum. (Found: C, 52·23; H, 5·10. $C_{23}H_{26}O_8NBr$ requires C, 52·67; H, 4·96 per cent).

The *hydrochloride* crystallises in clusters of needles, m.p. 241°, even from dilute solutions. It suffered no loss of weight on drying at 110° over P_2O_5 in vacuum. (Found: Cl, 6·01. $C_{23}H_{26}O_8NBr$, HCl requires Cl, 6·33 per cent).

The *hydrobromide* crystallises from hot water in needles, m.p. 225°. [Found: Br(HBr), 13·05. $C_{23}H_{26}O_8NBr$ HBr requires Br (HBr), 13·22 per cent].

The *picrate* crystallises from alcohol in bright yellow plates, m.p. 153°.

The *platinichloride* separated out as pale yellow prisms, m.p. 198° (decomp.). [Found: Pt, 13·29. $(C_{23}H_{26}O_8\ NBr,\ HCl)\ PtCl_4$ requires Pt, 13·38 per cent].

The *methyl ester* was prepared by saturating a suspension of bromonarceine (1 g.) in cold methanol (10 c.c.) with dry HCl, standing for 12 hours and then diluting it with water and making alkaline with sodium carbonate. The precipitate crystallised from dilute alcohol in colourless plates, m.p. 114°. (Found: C, 53·37; H, 5·61. $C_{24}H_{28}O_8NBr$ requires C, 53·53; H, 5·2 per cent).

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Synthesis of Coumarins from Phenols and β-Ketonic Esters. Part III. Use of Various Condensing Agents.

BY DUHKHAHARAN CHAKRAVARTI.

In the condensation of various mono-, di- and trihydric phenols with β-ketonic esters it has been observed that coumarins are produced using sulphuric acid as the condensing agent but phosphorus pentoxide may produce either coumarins or chromones (Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129, 407, 619; 1932, **9**, 25, 31, 389; *cf.* Robertson and co-workers, *J. Chem. Soc.*, 1931, 1256, 1877, 2426; 1932, 1180, 1681). Excepting in the case of condensation of β-naphthol with unsubstituted acetoacetic ester (Dey and Lakshminarayanan, *J. Indian Chem. Soc.*, 1932, **9**, 153) no other case has been detected where a chromone is formed even in traces using sulphuric acid. Attention was, therefore, directed towards the investigation of the part played by phosphorus pentoxide in the formation of chromones as well as towards the possibility of substituting any other condensing agent for phosphorus pentoxide for the synthesis of chromones. Thus various acidic, basic and neutral condensing agents like phosphoric acid, zinc chloride, hydrochloric acid gas, sodium ethoxide, boric anhydride and sodium acetate have been tried. Zinc chloride and hydrochloric acid gas were previously used by investigators in Pechmann's reaction for the synthesis of coumarins. It is remarkable to note that if condensation takes

place then coumarins are always formed (as shown in the table in the experimental part) and all attempts to find a substitute for phosphorus pentoxide have failed. This singular behaviour of phosphorus pentoxide is noteworthy.

It may also be noted that sulphuric acid in Pechmann's reaction may with advantage be replaced by phosphoric acid particualrly in the case of polyhydric phenols (*e.g.*, resorcinol, orcinol, pyrogallol and phloroglucinol), when better yields and purer products are obtained. It has also been found by the author that in Bülow's reaction, which is similar to Pechmann's reaction, the condensation of phenols with β-diketones may also be effected with advantage using sulphuric acid or better phosphoric acid.

Experimental.

β-Methylumbelliferone (7-hydroxy-4-methylcoumarin). (*a*) *With phosphoric acid.*—Phosphoric acid (*d* 1·75, 30 c.c.) was added to a mixture of resorcin (10 g.) and acetoacetic ester (8 c.c.) and the solution left overnight, when crystals separated. The mixture was poured into water and the solid crystallised as needles from dilute alcohol, m.p. 185-86°, yield 80%.

(*b*) *With sodium acetate.*—A mixture of resorcin (7 g.) and acetoacetic ester (5 g.) was heated for about 10 hours at 190°-200° with fused sodium acetate (20 g.). The mass was then washed with water and crystallised from rectified spirit, m.p. 185°, yield 72%.

(*c*) *With boric anhydride.*—Resorcin (7 g.), acetoacetic ester (5 g.) and boric anhydride (20 g.) were heated on the water-bath for about 10 hours. The mixture was then treated with dilute sodium carbonate solution and the residue crystallised from dilute alcohol, m.p. 185°, yield 50%.

(*d*) *With sodium ethoxide.*—Resorcin (5 g.) was added to a solution of acetoacetic ester (5 g.) in an alcoholic solution of sodium ethoxide (1 g. of sodium in 25 c. c. of alcohol) and the solution heated for 15 minutes on the water-bath, when the sodium salt separated. The solution was diluted with water, acidified with hydrochloric acid and the precipitate crystallised from dilute alcohol, m.p. 185°, yield 54%.

The melting point of the products in all these cases was not depressed when mixed with β-methylumbelliferone. The acetyl

derivatives, prepared by heating the substances with acetic anhydride and fused sodium acetate, crystallised in needles from dilute alcohol, m.p. 150°, identical with the acetyl derivative of β-methylumbelliferone of Pechmann.

7-*Hydroxy*-4-*methylcoumarin*-3-*acetic ester* was prepared by the condensation of resorcin (10 g.) and ethyl acetosuccinate (10 g.) in presence of phosphorus pentoxide (40 g.). The reaction set in with much evolution of heat on warming on the water-bath. After 15 minutes the product was treated with ice-cold water and the precipitate washed with dilute sodium carbonate solution and crystallised from alcohol, m.p. 163°, the m. p. being not depressed when mixed with a specimen prepared in presence of sulphuric acid (Banerjee, *J. Indian Chem. Soc.*, 1931, **8**, 777). The identical compound was also obtained by condensing resorcin (3 g.) with ethyl acetosuccinate (4 g.) using phosphoric acid (15 c.c.)

5-*Hydroxy*-4:7-*dimethylcoumarin*-3-*acetic ester*.—It was prepared by adding concentrated sulphuric acid (10 c.c.) to a mixture of orcinol (4 g.) and ethyl acetosuccinate (5 g.) in the cold. It was isolated as usual and crystallised from rectified spirit in colourless plates, m.p. 198-200°. (Found: C, 64·9; H, 5·4. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8 per cent).

The identical compound was also obtained by the condensation of orcinol (10 g.) with ethyl acetosuccinate (10 g.) in presence of phosphorus pentoxide (30 g.). The reaction was complete on heating on the water-bath for 15 minutes, when the product was treated with ice-cold water and the precipitate washed with dilute sodium carbonate solution and crystallised from alcohol, m. p. 198-200°, the m. p. being not depressed when mixed with a specimen of the compound prepared above using sulphuric acid. The same compound was also obtained by condensing orcinol (5 g.) with ethyl acetosuccinate (4 g.) using phosphoric acid (20 c. c.).

7:8-*Dihydroxy*-4-*methylcoumarin*-3-*acetic ester* was prepared by the condensation of pyrogallol with ethyl acetosuccinate in presence of sulphuric acid in the usual manner. It was isolated as usual and crystallised from rectified spirit in colourless needles, m. p. 186°. (Found: C, 60·2; H, 4·9. $C_{14}H_{14}O_6$ requires C, 60·43; H, 5·04 per cent).

The compounds, prepared with different condensing agents, are tabulated below.

Reactants.	Condensing agent.	Product.	M. p.
Orcin + acetoacetic ester	H_3PO_4	5-Hydroxy-4 :7-dimethyl-coumarin	250°
Pyrogallol + acetoacetic ester	H_3PO_4	7 :8-Dihydroxy-4-methyl-coumarin	235°
Phloroglucinol + acetoacetic ester	H_3PO_4	5 :7-Dihydroxy-4-methyl-coumarin	285°
Pyrogallol + phenylacetoacetic ester	H_3PO_4	7 :8-Dihydroxy-3-phenyl-4-methylcoumarin	268°
Resorcin + benzoylacetic ester	H_3PO_4	7-Hydroxy-4-phenylcoumarin	240°
Pyrogallol + benzoylacetic ester	H_3PO_4	7 :8-Dihydroxy-4 phenylcoumarin	188°
Resorcin + benzylacetoacetic ester	H_3PO_4 or Na acetate or Na ethoxide	7-Hydroxy-3 benzyl-4-methylcoumarin	224°
Resorcin + methylacetoacetic ester	H_3PO_4 or Na acetate. or Na ethoxide.	7-Hydroxy-3 :4-dimethylcoumarin	256°
α-Naphthol + acetoacetic ester	H_3PO_4 or Na acetate.	4-Methyl-1 :2-α-naphthapyrone.	168°
β-Naphthol + acetoacetic ester	Na acetate	4-Methyl-1 :2-βα-naphthapyrone and 2-methyl-1 :4-βα-naphthapyrone, forming the styrene derivative with benzaldehyde, m. p. 198°.	179°
p-Cresol + acetoacetic ester.	H_3PO_4	4:6-Dimethylcoumarin	150°

The author desires to express his grateful thanks to Prof. P. C. Mitter for giving full facilities to carry on this investigation in his laboratory.

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Nitration. Part V. Nitration of Monohalogenated Derivatives of Xylenes.

By Phuldeo Sahay Varma and K. S. Venkat Raman.

The nitro-derivatives of monohalogenated (*o*-, *m*-, and *p*-) xylenes have been obtained mostly by the replacement of the amino group by the halogen atom in the corresponding nitro-amino derivatives of xylenes (Ahrens, *Annalen*, 1892, **271**, 17 ; Bamberger and Reber, *Ber.*, 1913, **46**, 199 ; Blanksma, *Chem, Zentr.*, 1913, **I**, 1108; Noelting, Braun and Thesmar, *Ber.*, 1911, **44**, 2253). Only two nitro derivatives, 4-chloro-5-nitro-*o*-xylene, and 2-chloro-5-nitro-*p*-xylene, have been obtained by direct nitration by the action of concentrated nitric acid (Claus, Croneweg, *J. pr. Chem.*, 1894, *ii*, **43**, 257; *Compt. rend.*, 1933, **196**, 1896).

Tho nitro-derivatives of the halogenated xylenes have been obtained in good yields by nitrating the respective monohalogenated derivatives in presence of nitrosulphonic acid mixture, containing about 50% of fuming nitric acid, The following compounds have thus been prepared: (1) 4-chloro-6-nitro-*m*-xylene, (2) 2-chloro-5-nitro-*p*-xylene, (3) 4-bromo-6-nitro-*m*-xylene, (4) 2-bromo-5-nitro-*p*-xylene (5) 4-iodo-6-nitro-*m*-xylene and (6) 2-iodo-5-nitro-*p*-xylene. Of these the nitro-derivative of 2-iodo-*p*-xylene has been prepared for the first time and from analogy the new compound is probably 2-iodo-5-nitro-*p*-xylene.

Experimental

4-Chloro-6-nitro-m-*xylene*.—To 4-chloro-*m*-xylene (7 c.c.) and acetic anhydride (5 c. c.) nitrosulphonic acid mixture (9 c. c.) was added slowly and the flask cooled under tap-water from time to time. When the whole of the nitrating mixture was added, the mixture was refluxed on a water-bath for about 4 hours. The product after washing with water and then with sodium bicarbonate solution was extracted with benzene. After recrystallisation from ether it melted at 42° and was identified to be 4-chloro-6-nitro-*m*-xylene, yield 6·8 g.

2-*Chloro*-5-*nitro*-p-*xylene* was obtained in a similar way from 2-chloro-*p*-xylene (5 c. c.). The product crystallised from ether, m. p. 78°; yield 5·6 g. (Found: N, 7·47. $C_8H_8O_2NCl$ requires N,7·55 per cent). From the sodium bicarbonate extracts small quantity of 3-chloro-*p*-toluic acid, m. p. 200-2° were obtained, yield 0·4 g.

4-*Bromo*-6-*nitro*-m-*xylene* was obtained similarly from 4-bromo-*m*-xylene (5 c. c.), m. p. 57°, yield 5·2 g.

2-*Bromo*-5-*nitro*-p-*xylene*, m. p. 70°, can be obtained in the same way from 2-bromo-*p*-xylene (5 c. c.), yield 5·7 g.

4-*Iodo* 6-*nitro*-m-*xylene* can be obtained from 4-iodo-*m*-xylene (5 c.c.). It melts at 86°, yield 4·8 g.

2-*Iodo*-5-*nitro*-p-*xylene*.—To 2-iodo-*p*-xylene (3 c. c.) and acetic anhydride (3·5 c. c.), nitrosulphonic acid mixture (7 c. c.) was added drop by drop in about 15 minutes and then heated on a water-bath for about 2 hours. The product was subjected to the same treatment as mentioned above. It melts at 83°, yield 4·5 g. (Found: N, 4·98. $C_8H_8O_2NI$ requres N, 5·06 per cent).

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The Chemistry of Jute-lignin. Part VIII. Methylation of Lignin.

By Pulin Behari Sarkar.

Of the constituent groups that lignin contains, besides methoxyl, hydroxyl is the only group regarding the presence of which there seems to be no difference of opinion. Many investigators have carried out methylation and acetylation of lignin obtained from various sources. But the results of methylation so far available, scarcely show any concordance as regards the highest methoxyl value and the number of OH groups present in lignin, when a definite mol. wt. is assigned to it. Heuser and co-workers (*Cellulosechem.*, 1921, **2**, 81) methylated HCl-lignin from pine-wood with dimethyl sulphate and 10% NaOH at 60° and obtained a final product with 26·29 % methoxyl. The original lignin had a methoxyl content of 14·65 %, which means 4 OCH_3 groups in a mol. wt. of 846 for lignin provided, of course, it lost no methoxyl in the course of isolation. Now, 26·29% of OCH_3 in the fully methylated product corresponds to a figure which is less than 8 but more than 7 methoxyl groups, assuming that 846 represents the correct mol. wt. of lignin. Urban (*Cellulosechem.*, 1926, **7**, 73) employed 45 % KOH and dimethyl sulphate below 26° for the methylation of spruce-wood lignin and got a product with the highest methoxyl value (32·4%). Dimethyl sulphate and alkali under various conditions have been used by Holmberg and Wintzell (*Ber.*, 1921, **54**, 2471), Powell and Whittaker (*J. Chem. Soc.*, 1924, **125**, 357), Friedrich and Diwald (*Monatsh.*, 1925, **46**, 44) as well as by Fuchs and Daur (*Cellulosechem.*, 1931, **12**, 104) for the purpose of methylating different lignins but the results are all different.

It has been shown by the author (*J. Indian Chem. Soc.*, 1934, **11**, 691) that the dioxymethylene group is a common constituent of lignin and also that this group suffers partial decomposition during isolation by acid hydrolysis under usual conditions. As the percentage of OH thus appearing essentially depends on the extent to which the separated lignin loses its $O\text{-}CH_2\text{-}O$ group, obviously the methy-

lation value can never be expected to be the same. This is actually the fact. In order to get an idea of the exact number of OH groups in lignin, therefore, one should start with the genuine lignin with all the O-CH_2-O groups in tact. From this point of view, it was thought worth while to study in detail the methylation of jute-lignin to see how many OH groups it actually contains.

Jute-lignin, separated in the ordinary way, was methylated with dimethyl sulphate and KOH according to Urban's method (*loc. cit.*); the highest methoxyl value that could be reached (35—36%) was not in any simple ratio with its original methoxyl content, taking as before 830 as the mol. wt. of jute-lignin. But when lignin isolated at low temperature taking the same precautions as mentioned in a previous paper (*ibid.*, 1934, **12**, 691) was similarly methylated, the final methoxyl value was always 34·51%.

In a previous paper (*J. Indian Chem. Soc.*, 1935, **12**, 168) it was stated that on comparing the methoxyl values of raw and delignified jute, it was found that jute-lignin isolated at room temperature in the usual way suffered a loss of 1·96% of methoxyl. The lignin thus separated had 16·41% OMe whilst it should have contained 18·37% OMe, had all the methoxyls remained in it. By isolating lignin by the modified method of the author (*loc. cit.*) it has now been possible to obtain a sample of lignin with 19·18% of OMe which fact, therefore, shows its genuine character. Accepting 830 as the mol. wt. of jute-lignin, 5 methoxyl groups in the molecule means 18·66% of methoxyl; while actually 19·18% has been found. This sample had all the O-CH_2-O unaffected as it yielded 2·78 % of formaldehyde and was insoluble in dilute caustic alkalis. The latter fact shows that no free phenolic group was present in it; it did not reduce Fehling's solution. The figure 34·51% of methoxyl means 10 methoxyl in all, hence 5 additional OCH_3 groups have entered the molecule. Genuine jute-lignin, therefore, contains 5 OH groups.

In a previous communication (Sarkar, *J. Indian Chem. Soc.*, 1934, **11**, 568), it has been shown that the reducing action of lignin is due to two OH groups in the *ortho*-position attached to the benzene ring, formed as a result of splitting off of formaldehyde from the dioxymethylene group in jute-lignin during isolation and not to any aldehyde group. Further evidence has now been available to corroborate this view. Jute-lignin boiled with 28% sulphuric acid under reflux for 3-4 hours reduced Fehling's solution very readily. This was methylated in the usual way repeatedly until the methoxyl value was

constant. But the methylated product no longer reduced Fehling's solution. Had the reducing action of lignin been due to an aldehyde group, this would not have been the case.

In numerous estimations of methoxyl in jute-lignin by Zeisel's method (with Perkin's modification) it has always been observed that CH_3I first appeared at 92°-93°. This was also the case with vanillin and vanillic acid. This striking similarity indicates, therefore, that vanillin residue is present in lignin, which is in agreement with experimental facts. In other words, in jute-lignin OCH_3 is linked to the benzene ring, which has also been shown by Freudenberg and others (*Ber.*, 1929, **62**, 1554). In the case of methylated lignin, the CH_3I appeared at 84°-85°, from which fact it may be inferred that the methoxyl groups have during methylation entered not the benzene ring (as no free phenolic group was present in the original lignin) but the side-chain.

Genuine jute-lignin was boiled with 28% sulphuric acid under reflux for 3-4 hours but the methoxyl value remained unchanged. The same sample was boiled under reflux with 2*N*-alcoholic KOH for the same period but the lignin had the same methoxyl content as before, *viz.*, 19·18 %. This shows that all the methoxyl groups in jute-lignin are linked in the form of ether.

As the lignin after methylation was obtained in the form of a tarry mass which could not be purified without taking recourse to alkali boiling, it was not possible to detect any carboxyl group by methylation with dimethyl sulphate. The fully methylated product had practically the same methoxyl value even when it was boiled with 28 % sulphuric acid or alcoholic caustic potash under reflux for 3-4 hours.

Methylated jute-lignin was oxidised with 5*N*-nitric acid following the procedure of Phillips and Goss (*J. Amer. Chem. Soc.*, 1933, **55**, 3466) but no anisic acid could be detected in the oxidation products.

Experimental.

Methylation of lignin.—About 2 g. of very finely powdered lignin were intimately mixed with 25 c.c. of 45% KOH in a Nessler's tube fitted with a rubber cork, through which passed a mechanical stirrer and a separating funnel. Dimethyl sulphate (30 c.c.) was slowly added drop by drop within 3-4 hours to the solution maintained at 20-22° and stirred all the while. Next day the pasty mass obtained

by decanting the liquid, was boiled with dilute caustic soda to decompose the excess of dimethyl sulphate, washed thoroughly with water and dried at 105°. Methoxyl value was determined according to Zeisel's method. The same process of methylation was repeated three to four times until the methoxyl value was constant. The results are shown in Table I. It is worth mentioning here that at higher temperatures the methoxyl value rose up more slowly, thus at 60°, after successive methylations for 5 times, the methoxyl content was only 28·65%, while it required only 3 such treatments to reach the maximum figure at 20°. Further, it was found necessary to add 3 times the KOH Urban used in order to facilitate stirring. Before each fresh treatment with dimethyl sulphate it was essential to have the lignin in the pulverised form and mixed thoroughly with the caustic potash, otherwise the process had to be repeated a larger number of times to effect maximum methylation.

TABLE I.

	(*a*) Jute-lignin separated at room temperature.		(*b*) Jute-lignin isolated by the modified method.		(*c*) Sample (*b*) boiled with 28% H_2SO_4.	
No. of treatment.	OMe.	Temp. of 1st appearance of MeI.	OMe.	Temp. of 1st appearance of MeI.	OMe.	Temp. of 1st appearance of MeI.
	16·41%	92°–93°	19·18%	92°–93°	19·05%	92°–63°
1	20·87	...	28·34	84°–85°	26·87	84°–85°
2	24·85	84°–85°	33·56	,,	32·45	,,
3	32·54	,,	34·51	,,	36·70	,,
4	35·87	,,	34·32	,,	36·62	,,
5	35·68	,,	...	...	...	...

Samples (*a*) and (*c*) reduced Fehling's solution before methylation but not after. Sample (*c*) was dark coloured and fairly soluble in dilute caustic alkalis before treatment with dimethyl sulphate but the colour became light brown on methylation and also it was quite insoluble in alkali afterwards. All the methylated products were practically insoluble in the usual solvents. None melted within 300°.

Formaldehyde was estimated in the final product of sample (*b*) by the dimedone method (*J. Indian Chem. Soc.*, 1934, **11**, 691) and the figure after solubility correction was 2·36% which shows that the dioxymethylene group was unaffected during methylation.

TABLE II.

Genuine lignin from jute.		Genuine jute-lignin.		Methylated lignin of sample (*b*).	
Treatment.	OMe.	Treatment.	OMe.	Treatment.	OMe.
—	19·18%	—	...	...	34·51%
Boiled with 28% H_2SO_4	18·78	Boiled with 2N-alcoholic KOH for 3-4 hrs.	19%	Boiled with 28% H_2SO_4	34·24
				Boiled with alcoholic KOH	34·15

Oxidation of jute-lignin after methylation.—5 G. of the fully methylated lignin (with 34·51% methoxyl) and 50 c.c. of 5*N*-nitric acid were heated on a water-bath for 1/2 hour, cooled, filtered and washed. The ethereal extract of the filtrate on evaporation gave a syrupy liquid mixed with nitric acid. The small quantity of solid separated therefrom after the removal of nitric acid was found to be oxalic acid (m.p. 101°).

SUMMARY.

1. By methylating jute-lignin, it has been shown that it contains 5 OH groups in a molecular weight of 830.

2. As the reducing lignin no longer reduces Fehling's solution after methylation, it is concluded that jute-lignin contains no aldehyde group.

3. From the temperature at which CH_3I first appears, it is inferred that OCH_3 is linked to benzene ring in natural lignin.

4. All methoxyl groups in jute-lignin are of ether type, as also those entering the molecule on methylation.

5. By the oxidation of methylated jute-lignin no anisic acid could be detected.

6. No information regarding the carboxyl group was obtained from the methylation of lignin as alkali boiling could not be avoided during purification.

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The Chemistry Jute-lignin. Part IX. Acetylation of Lignin.

By Pulin Behari Sarkar.

In the previous paper it has been shown by the author that no definite conclusion regarding the number of hydroxyl groups in lignin can be drawn from the results of methylation of lignin separated in the usual way, in view of the fact that new OH groups appeared owing to the partial decomposition of the dioxymethylene group present in lignin. It was further pointed out that five additional methyl groups entered the molecule of genuine lignin when it was methylated with dimethyl sulphate and alkali. To confirm the results obtained by the methylation of jute-lignin, it was acetylated.

Like methylation, acetylation results of lignin by different workers seldom agree ; many of these do not even corroborate the methylation data. Thus, the maximum methoxyl value of Heuser and co-workers (*Cellulosechem.*, 1921, **2**, 80) corresponded to about four OH groups, whilst their acetylation data (*ibid.*, 1924, **5**, 13) indicate the presence of six OH groups in the molecule. The acetyl content of HCl-lignin varied considerably with the source of lignin as has been shown by Pringsheim and Mangus (*Z. physiol. Chem.*, 1919, **105**, 179). Various lignins have been acetylated by Powell and Whittaker (*J. Chem. Soc.*, 1924, **125**, 357), Phillips (*J. Amer. Chem. Soc.*, 1927, **49**, 2037) as well as by Fuchs and Horn (*Ber.*, 1929, **62**, 2647), but their highest acetylation values do not at all agree with one another. It is difficult to say how far it is due to the difference in technique adopted and to what extent to the difference in the source whence the lignin was obtained.

Of the usual methods available for acetylation, acetic anhydride in presence of pyridine was found to be the best, the highest acetyl value being obtained by two successive treatments. The highest acetic acid content has been found to be 26·45%, which means five OH groups in a molecular weight of 830 for lignin, the theoretical value being 28·85%. Thus, in the case of jute-lignin the results of acetylation agree quite well with the methylation data.

As expected, by acetylating ordinary HCl-lignin and genuine lignin after boiling with 28% sulphuric acid for 3-4 hours under reflux, higher percentage of acetic acid was obtained in both cases. The results are shown in Table I.

Reducing lignin (genuine lignin boiled with moderately strong HCl or 28% sulphuric acid) on acetylation no longer reduced ammoniacal silver nitrate, showing conclusively the absence of aldehyde group in jute-lignin. This confirms the previous observation of the author (*J. Indian Chem. Soc.*, 1934, **11**, 691) that the reducing action of lignin is due to the presence of 2 hydroxyl groups in the *ortho*-position attached to the benzene rings formed as a result of partial degradation of lignin in respect of its dioxymethylene group. The reducing action of acetylated lignin on Fehling's solution could not be tested because of the fact that the warm caustic alkali hydolysed the acetyl groups readily and the product reduced Fehling's solution.

The dioxymethylene group has been found to remain unaffected during acetylation, as will be seen from the formaldehyde-content of the acetylated lignin.

Very little improvement in colour was observed on acetylating lignin ; so the view of Pringsheim and Mangus (*loc. cit.*) that the dark colour of separated lignin was due to the loss of acetyl group, does not appear to be justified. Nor did the acetylated lignin go into solution in pyridine as was observed by them.

The fact that acetic acid corresponding to five acetyl group entering a molecule of 830 was obtained, lends further support to the author's former view that this figure actually represents the molecular weight of jute-lignin. The methoxyl value (Zeisel's method) of the acetylaled product was found to be 15·32%, which shows that all the five methoxyl groups present in original lignin are also present in the acetylated product.

To test for the presence of ethylenic double bond, jute-lignin was shaken mechanically with metallic palladium in a closed chamber containing hydrogen (connected to a manometer) for 4 to 5 hours, but no absorption of hydrogen was observed. This fact further corroborates the results obtained by the author by the chlorination of lignin (*J. Indian Chem. Soc.*, 1934, **11**, 777) when the ratio of chlorine evolved as HCl to the chlorine combined with the lignin, was shown to be very approximately equal to 1 : 1.

Attempts to measure the iodine value of lignin as done by Mehta (*Biochem. J.*, 1925, **19**, 958) with IBr or 1Cl proved futile as small

amount of these reagents was absorbed by saturated benzene compounds like phenol, anisol, vanillin and others (Table II) and as the results with lignin was too low, and of the same order as with vanillin, it might be inferred that no ethylenic double bond in the side-chain is present in jute-lignin.

The iodoform-yielding complex in jute-lignin appears in all probability to be a side-chain consisting of CH_3-CO- or CH_3-CHOH- groupings as observed by the author (*J. Indian Chem. Soc.*, 1934, **11**, 691). Raw jute and HCl-lignin but not delignified jute, gave iodoform at room temperature with iodine and caustic soda. This shows that the iodoform-yielding complex is characteristic of lignin and not of cellulose; and further, this group remains in tact during the isolation of lignin. The distillate obtained by the acid or alkali distillation of jute-lignin, or its chloro-derivative, responded to the colorimetric test for CH_3-CO- by Goswami and others (*J. Indian Chem. Soc.*, 1934, **11**, 773), but it has not yet been possible to identify the volatile substance.

Following the procedure of Böesenken and Sloof (*Proc. Amsterdam Academy of Sci.*, 1932, **35**, 170) who prepared a cyclic compound of pyrocatechol by treating it with acetone in presence of P_2O_5 below 10°, it has been possible to obtain a similar compound with jute-lignin after expelling all the formaldehyde from it in the usual manner. The black starting material became light gray in colour and was no longer soluble in dilute caustic soda. It did not exhibit any reducing property towards Fehling's solution. This proves the presence of two OH groups in the *ortho*-position in lignin formed as a result of the loss of formaldehyde and further corroborates the author's results of methylenation of jute-lignin (*J. Indian Chem. Soc.*, 1934, **11**, 691).

Experimental.

Acetylation of jute-lignin.—About 2 g. of very finely powdered jute-lignin (dried at 105°) was heated on a water-bath for 2-3 hours with 25 c.c. of a mixture of acetic anhydride (12 c.c.) and pyridine (88 c.c.). The acetylated product obtained after pouring the solution into water, was washed with water and pyridine. It was dried at 105°. To ensure complete acetylation, the process was repeated a second time.

Estimation of acetic acid.—About 0·5 g. of the finely powdered acetylated product was taken in a flask and 5 c.c. of concentrated sulphuric acid was added to it, it was corked and shaken from time to time gently to ensure thorough mixing. After 24 hours, 200 c.c. of water were added to it and the liquid distilled in steam very slowly until the distillate was neutral to litmus. To obtain concordant results, it was necessary to use an ammonium distillation bulb in the flask containing the liquid and barium hydroxide in the steam generator. The former prevents any mechanical carriage of sulphuric acid and the latter frees the steam from carbonic acid gas. The distillate was transferred to a measuring flask as soon as possible to avoid absorption of carbon dioxide from air and acetic acid estimated by titration in the usual way.

TABLE I.

Sample acetylated.	Acetic acid.	Mean.
(*a*) Jute-lignin prepared in the usual way.	32·0 % 33·5	32·75 %
(*b*) Jute-lignin prepared by the modified method.	28·9 30·0	29·45
(*c*) Sample (*b*) boiled with 28% sulphuric acid for 4 hours under reflux.	34·20 35·52	34·86

None of the acetylated products dissolved in any solvent nor melted within 300°. Sample (*c*) was fairly soluble in dilute caustic soda before acetylation but was insoluble afterwards, showing the absence of free phenolic group.

The methoxyl value of sample (*b*) was found to be 15·32%; the molecular weight of the acetylated lignin being 1040 (taking 830 as the molecular weight of the original lignin) this figure indicates the presence of 5 methoxyl groups in it. These were also present in the original lignin. Formaldehyde was estimated in the acetylated product by the dimedone method and the yield after solubility correction was 2·16%. This shows that the dioxymethylene group as well remained unaffected during acetylation.

Absorption of IBr *and* ICl *by jute-lignin.*—As will be found in the following table, saturated aromatic compounds absorb a small amount of these reagents just like lignin. About 0·3 g. of the substance was taken in a stoppered conical flask and 10 c.c. of IBr or ICl

solution in glacial acetic acid was added and kept for about an hour in a dark place in the usual way. Excess of the reagent was titrated with thiosulphate after adding sufficient KI solution. IBr and ICl behaved similarly. The results are shown in Table II.

TABLE II.

Substance.	Original titre (thio).	Final titre (thio).	Substance.	Original titre (thio).	Final titre (thio).
Phenol	21·50 c.c.	14·30 c.c.	Resorcinol	20·8 c.c.	10·60 c.c.
Anisol	,,	14·20	Aspirin	,,	20·20
Benzene	,,	21·50	*p*-Cresol	,,	13·4
Vanillin	,,	17·55	*p*-Cresol methyl ether	,,	15·0
Benzoic acid	,,	21·50	*m*-Cresol	,,	11·45
Piperonylic acid	,,	21·45	*m*-Cresol methyl ether	,,	13·70
Lignin	,,	17·50	*cyclo*Hexane	,,	20·45
Phloroglucinol	,,	9·0	*cyclo*Hexanol	,,	16·10

SUMMARY.

1. By the acetylation of jute-lignin, it has been shown that it contains 5 OH groups; methylation and acetylation results agree very well.

2. Acetylation value of genuine lignin further confirms the view that jute-lignin has a mol. wt. of 830.

3. As the acetylated lignin no longer shows any reducing action, it is concluded that jute-lignin contains no aldehyde group.

4. As jute-lignin absorbs no hydrogen in presence of metallic palladium, it is inferred that it has no ethylene linkage.

5. Slight absorption of IBr or ICl by jute-lignin does not prove the presence of a double bond in the side-chain.

6. Acetone compound of jute-lignin has been prepared, which corroborates the author's view regarding the $O\text{-}CH_2\text{-}O$ group in lignin as shown by the methylenation of jute-lignin.

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552

The Viscosity of Titanium Dioxide Sol in Presence of Electrolytes.

By S. M. Mehta and (Miss) Olive joseph.

Viscosity has been recognised as an important property which is very sensitive to changes in a colloidal system. It has been utilised for the study of three important characteristics of colloidal systems, *viz.*, (*i*) the change which takes place during gelation, (*ii*) the rate of coagulation and (*iii*) the degree of hydration of the colloidal particles.

Prakash and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 391) and Prasad, Mehta and Desai (*J. Phys. Chem.*, 1932, **36**, 1384) measured the viscosity of certain gel-forming mixtures to recognise different stages in the process of gelation. They explained the variation in viscosity on the changes in hydration of the colloid particles. Fernau and Pauli (*Kolloid Z.*, 1917, **20**, 20), Ostwald (*Trans. Faraday Soc.*, 1913, **9**, 35) and Dhar and co-workers (*Kolloid Z.*, 1926, **38**, 253 ; 1928, **44**, 225 ; 1929, **48**, 43 ; *J. Phys. Chem.*, 1926, **30**, 1646) have all pointed out that the electrical charges carried by the colloid particles determine the degree of hydration of the particles and the changes in viscosity of a sol. Hatschek (*Kolloid Z.*, 1920, **27**, 163) has shown how the hydration factor of a colloid particle can be calculated from the results on the measurements of viscosity.

Freundlich and Ishizaka (*Trans. Faraday Soc.*, 1913, **9**, 66), Pauli (*ibid.*, p. 64), Smoluchowski (*Kolloid Z.*, 1916, **18**, 190), Kawamura (*J. Coll. Sci. Imp. Univ. Tokyo*, 1908, **8**, 25) and numerous other investigators have used viscosity to measure the rate of coagulation of a sol. Gann (*Koll. Chem. Beih.*, 1916, **8**, 64) who measured the changes in viscosity of aluminium oxide sol in presence of different amounts of electrolytes found that the autocatalytic nature of coagulation can be inferred from the viscosity-time curves.

Recently Joshi and co-workers (*J. Indian Chem. Soc.*, 1933, **10**, 329, 589 ; 1934, **11**, 173) have shown that autocatalysis though prevalent under certain conditions cannot be considered as a general characteristic of the coagulation phenomenon. They have also shown that on the addition of electrolytes, the viscosity shows an

initial diminution followed by a slow increase and that the viscosity-time curves *are not continuous* but show well marked breaks (Joshi and co-workers, *J. Indian Chem. Soc.*, 1933, **10**, 329 ; 1934, **11**, 133, 555, 573, 797). Patel and Desai (*Trans. Faraday Soc.*, 1933, **26**, 177) have found that the purity and the concentration of the colloid are necessary factors in determining the autocatalytic nature of the coagulaiton process. In the present investigation the changes in viscosity of titanium dioxide sol with time when electrolytes are added to the sol dialysed and diluted to different extents have been studied with a view to examine the validity of the above views.

Experimental.

The sol was prepared by the peptisation of titanium hydroxide by hydrochloric acid. The titanium hydroxide was first precipitated by adding ammonium hydroxide and then washed with hot water till free from ammonia. It was suspended in a large volume of water and boiled. At intervals, 2*N*-hydrochloric acid was added till the sol was quite clear. The volume of the sol was kept constant by replacing the evaporated water from time to time. The sol was dialysed in a parchment bag in continuously running water, the level of water in the outside vessel being kept constant. During dialysis, no titanium was detected in the dialysate.

The colloid content of the sol was estimated by taking 25 c.c. of the sol and adding to it a concentrated solution of ammonium chloride in excess to coagulate it. The sol was heated on a water-bath at 70° to hasten coagulation. The precipitate was filtered, dried in an air-oven, ignited in a silica crucible and weighed as TiO_2. The concentration of the sol was found to be 2·912 g. of colloidal TiO_2 per litre.

Scarpa's method (*Gazzetta*, 1919, **40**, 271) modified by Farrow (*J. Chem. Soc.*, 1912, **101**, 347) and improved upon by Prasad, Mehta and Desai (*loc. cit.*) was used. The viscometer along with the guard tube was enclosed in an electrically heated thermostat maintained at 33° ± 0·02°.

The apparatus being standardised, 10 c.c. of the sol were introduced into the viscometer and suction at a pressure of 15 cm. of water, which was kept constant throughout the investigation, was applied. When the level of the liquid reached the lower mark, a stop-watch was started and the time of rise, t_1 from the lower to the upper mark was

noted. The viscometer was next connected to the atmosphere and the time of fall, t_2 from the upper to the lower mark was also noted. The viscosity of the sol was calculated from the formula,

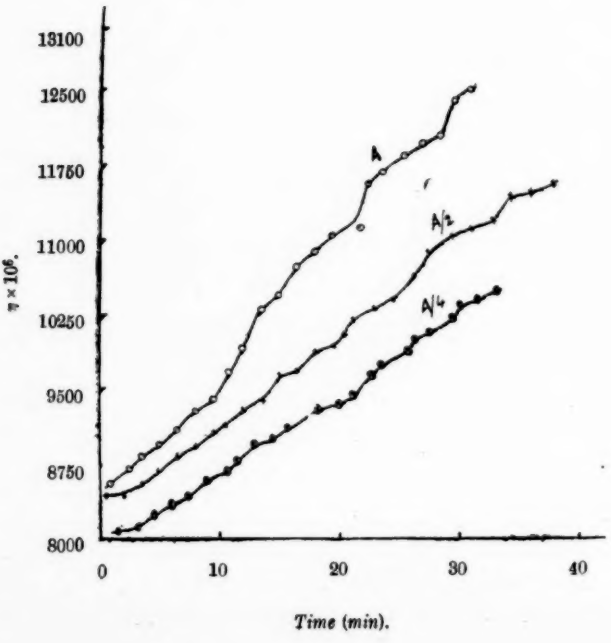
$$\eta = K\left(\frac{t_1 t_2}{t_1 + t_2}\right)$$

where K is a constant which was determined by finding out $t_1 t_2/t_1 + t_2$ for pure water whose absolute coefficient of viscosity at 33° is known and it was found to be 0·001136.

For coagulation 5 c.c. of the sol were taken in a test tube and in another the requisite amount of the electrolyte was diluted to 5 c.c. by adding distilled water. The total volume of the sol + electroiyte was always 10 c.c.

FIG. 1.

$AlCl_3$ *and undialysed sol.*



When the electrolyte was added to the sol, a second watch was started. This gave the time since mixing at which the time of rise and fall in the viscometer was measured. The mean of the time at which the mixture was made to rise and that at which it reached the lower mark while falling, was reckoned as the time at which the viscosity reading of the mixture was taken.

The electrolytes employed were the chlorides of potassium, magnesium and aluminium. Their concentrations were so selected that the time required for coagulation was about an hour and a quarter. The original sol is designated A and the twice and four times diluted ones, $A/2$ and $A/4$. All the results are not given; only a few selected ones are shown graphically in Fig. 1-3 for illustration.

FIG. 2.

KCl + *sol dialysed for* 9 *days.*

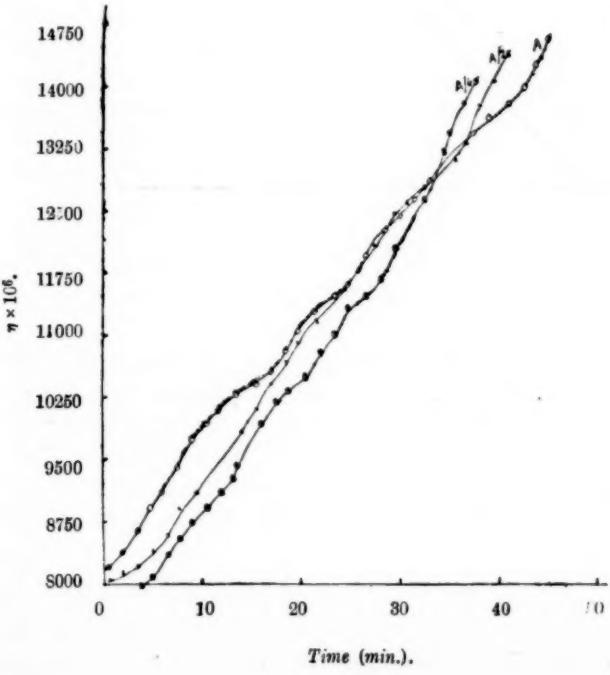
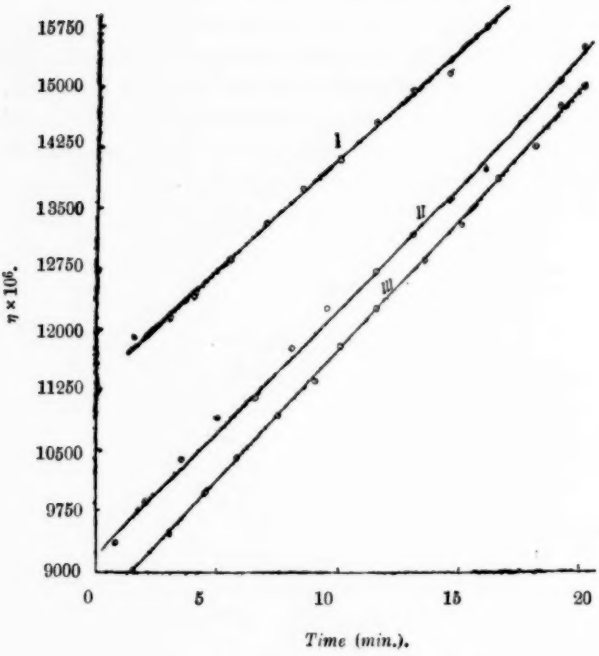


FIG. 8.

A-sol dialysed for 20 *days.*



I—$AlCl_3$: II—$MgCl_2$: III—KCl.

The p_H of the various samples of the sol was determined by the indicator method. 10 C.c. of the sol were coagulated by potassium chloride (0·5 g.) and 1 c.c. of bromophenol-blue was added to the supernatant liquid. The tint thus obtained was compared with that of the standards prepared from the B.D.H. universal buffer mixture. The values of p_H thus obtained did not differ from those obtained with the sol using Walpole's comparator method.

The electrical conductivity of each of the samples was also determined by Kohlrausch's method. The results are given in the following table in which k denotes specific conductivity.

TABLE I.

Specific conductivity and p_H.

Sol dialysed for	*A*		*A/2*		*A/4*	
	$k \times 10^3$.	p_H.	$k \times 10^3$.	p_H.	$k \times 10^3$.	p_H.
0 days	34·56	2·4	18·07	2·5	9·25	2·6
3	7·26	2·8	3·77	3·1	2·02	3·3
6	3·84	3·0	1·96	3·3	1·55	3·7
9	3·12	3·5	1·68	3·7	1·33	3·9
12	2·45	3·7	1·51	3·8	1·23	4·9
15	1·96	4·0	1·37	4·2	1·10	4·3
20	1·79	4·1	1·19	4·3	0·98	4·4
25	1·63	4·2	1·08	4·5	0·85	4·8

DISCUSSION.

It will be seen from the curves in Fig. 1—3 that the viscosity of the titanium dioxide sol to which an electrolyte is added increases with time. This increase in viscosity may be due to (*i*) an increase in size of the colloid particles due to coagulation and (*ii*) an increase in their hydration due to a diminution in their electric charge. But it is to be observed that the curves obtained with this sol dialysed only for a few days are *periodic* and do not show a continuous increase in viscosity with time. As the sol gets purer due to continued dialysis, the *periodic* nature of the curves disappears. This fact is illustrated in the following table in which P, P_1, P_2 and P_3 represent diminishing periodicity in the curves and N denotes its absence.

TABLE II.

Sol dialysed for	KCl			$MgCl_2$			$AlCl_3$		
	A.	*A/2*.	*A/4*.	*A*.	*A/2*.	*A/4*.	*A*.	*A/2*.	*A/4*.
0 days	P	P	P_2	P_2	P_3	P_3	P_3	P_3	P_3
3	P	P	P_2	P_2	P_3	P_3	P_3	P_3	N
6	P_1	P_1	P_2	P_2	P_3	N	P_3	P_3	N
9	P_1	P_1	P_2	N	N	N	N	N	N
12	N	N	N	N	N	N	N	N	N
15	N	N	N	N	N	N	N	N	N
20	N	N	—	N	N	—	N	N	—
25	N	—	—	N	—	—	N	—	—

This sort of *periodic* or discontinuous nature of the viscosity-time curves was also observed by Joshi and co-workers (*loc. cit.*) in the coagulation of arsenious sulphide, antimony sulphide and certain lyophobic sols. The results obtained in this investigation are an independent cofirmation of the observations of the above investigators.

The above table also illustrates that the discontinuous nature of the curves becomes less marked as the sol is diluted. With $A/4$ sols the discontinuity in the curves is hardly perceptible. This is in accordance with the observations of the above investigators who found that the viscosity-time curves are periodic or discontinuous in the slow region of coagulation. The coagulation of particular samples of the sol by the same amount of an electrolyte is more rapid, the greater the dilution.

It will be noticed in Table II that the discontinuous nature of the viscosity-time curves is more marked with potassium chloride than with magnesium chloride or aluminium chloride. This may be attributable to the increased rate of coagulation of the sol with the latter electrolytes.

Table I shows that the specific conductivity and hydrogen ion concentration of the sol diminish both on dilution and dialysis. It would appear that this accounts for the rapidity of coagulation with dilution and dialysis which is a consequence of the decrease of the peptising ions.

The autocatalytic nature of the coagulation process as demonstrated by the "**S**" shape of the viscosity-time curves disappears as the sol is progressively dialysed: the curves for the sol dialysed for nine days or more do not have an "**S**" shape. This is in confirmation of the observations made in the previous communication (*J. Indian Chem. Soc.*, 1933, **11**, 177) that the purity of the sol plays an important part in determining the autocatalytic nature of its coagulation.

Summary.

1. The changes in viscosity of the titanium dioxide sol, dialysed and diluted to different extents, with time when electrolytes are added to it have been studied using Scarpa's method with modifications.

2. It is found that the viscosity of the sol increases with time and that the viscosity-time curves are periodic or discontinuous in the slow region. This is in agreement with the observations of Joshi and co-workers.

3. The specific conductivity and hydrogen ion concentration of the sol diminish both on dilution and dialysis thus accounting for the rapidity of coagulation as a consequence of the decrease of the peptising ions.

4. The autocatalytic nature of the coagulation process as demonstrated by the "**S**" shape of the viscosity-time curves disappears as the sol is progressively dialysed in confirmation of the observations made in a previous communication by the authors.

The authors desire to express their thanks to Dr. Mata Prasad for making useful suggestions.

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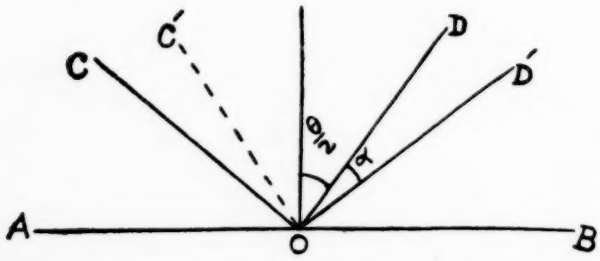
A Modified Photographic Method for Substances of Small Rotatory Dispersion.

BY R. PADMANABHAN.

The method usually adopted for measuring optical rotatory dispersion in the ultraviolet is to pass light from a polychromatic source through a spectro-polarimeter and take photographs for various settings of the analyser (Lowry, *Proc. Roy. Soc.*, 1908, **A**, **81**, 472). The wave-length at which extinction takes place is measured when the polarimeter consists simply of two nicols as polariser and analyser or, and this is the more usual case, in the case of a two-field instrument, the wave-length having equal intensity in the two halves of the spectrum is determined. In practice it is found that instead of a single wave-length being extinguished at a time, a dark band is obtained the width of which is determined by numerous factors such as the rotatory dispersion of the material under investigation, the magnitude of its rotation, the dispersion of the spectrograph used and the intensity distribution of the light source. The wave-length of the middle point of the band is taken as the required wave-length corresponding to the analyser setting but this is obviously unsatisfactory because of the usual shape of the rotatory dispersion curves. The error involved, however, will be negligible if the band is quite

narrow and well defined which will be the case for substances of large rotation and normal dispersive power. In the case of substances for which the variation of optical activity with wave-length is small, a wide band will be obtained although one might have an appreciable thickness of the substance and the readings will, therefore, tend to become inaccurate. The usual photographic method, therefore, fails for substances of small optical rotatory dispersion. The same arguments apply also to the common case where a two-field polarimeter is used, the only difference being that instead of a broad band, there is observed a large region of the spectrum having the two halves of nearly equal intensity.

FIG. 1.



Thus in Fig. 1, if AB represents the principal plane of the analyser and OC, OD represent the planes of polarisation of the two beams corresponding to the two fields of the polariser, after passing through the the substance for a particular wave-length λ, it follows that if OC and OD sustend equal angles on AB, then that wave-length will have equal intensity in the two halves of the spectrum. If, for a neighbouring wave-length λ_2, the corresponding planes of polarisation are rotated through an angle 'α' to the positions C'O and D'O, the ratio between the intensities in the two halves will be given by the expression,

$$\frac{\mathrm{Sin}^2(\theta/2 + \alpha)}{\mathrm{Sin}^2(\theta/2 - \alpha)}$$

where θ is the half-shadow angle. In order to enable an accurate measurement of the wave-length of equal intensity to be made, this expression must be as different from unity as possible for wave-lengths on either side of λ_1. This means that α must have a high value

which will be the case if (*a*) the substance has initially a high rotation and (*b*) it has a high dispersive power. The initial rotation can be increased by increasing the thickness but this is of limited utility since the light transmission is also thereby reduced. However, in the case of a substance having little or no rotatory dispersion the two halves of the spectrum will have nearly equal intensity over a large range of wave-lengths rendering it difficult to spot out the wave-length of equal intensity and increasing the thickness does not help very much in removing the difficulty. This trouble was experienced in the case of β-pinene whose rotatory dispersion curve runs almost parallel to the axis of wave-lengths in the visible and in the near ultraviolet. The usual procedure in such cases will be to isolate light of a particular wave-length by the use of a monochromator or by means of a suitable filter and make a visual observation. But in case the region of small rotatory dispersion lies in the ultraviolet as in the case of sabinene (Padmanabhan and Jatkar, *J. Amer. Chem. Soc.*, 1935, **57**, 334) this method is not applicable and either the usual photographic method is followed with a densitometer to determine the wave-length of equal intensity (Lowry and Vermon, *Proc. Roy. Soc.*, 1928, **A**, **119**, 706) or a quartz monochromator can be employed in conjunction with a photo-electric cell. In any case additional equipment is needed and hence the following method was devised which does not suffer from this disadvantage.

The method consists in determining the rotatory dispersion of the substance under test having a small variation of optical activity with wave-length, along with a suitable thickness of another optically active material having normal dispersive power and a fairly large rotation to start with the usual photographic method being used. Polarimeter tube end-plates of quartz come in very handy for this purpose. The wave-length of equal intensity now becomes easily measurable. A subtraction of the rotation of the quartz plate due to this wave-length, which can be determined either experimentally or from the data given by Lowry and Coode Adams (Bruhat *Trans. Faraday Soc.*, 1930, **26**, 400), gives the rotation due to the substance alone. The readings thus obtained are more accurate than it is possible with the older method. The proper sign and thickness of the quartz plates to be used in conjunction with the substance have to be determined by a few preliminary experiments. It is advisable not to use a greater thickness of quartz than necessary to obtain a

setting easily measurable on the travelling microscope because, if too great a thickness is used, although the setting becomes sharper, a small error in measurement corresponds to a larger difference in the optical rotation of the substance under test. This method has another advantage also. While taking readings near the limit of transmission, it is often observed, especially on the ultraviolet side of the extinction position, the increase in intensity with diminishing wave-length is so feeble that there is a large gap in the spectrum and the measurement consists in locating the middle point of the gap. By the use of a second optically active substance in conjunction, this gap is considerably reduced since the variation in intensity with wave-length is greater and hence the measurement can be pushed a little further in the ultraviolet.

Experimental.

The following table shows the measurements obtained in an actual case with *l*-β-pinene. The experimental details have already been published (Padmanabhan and Jatkar, *loc. cit.*).

Table I.

Length of polarimeter tube used = 2·5 cm.

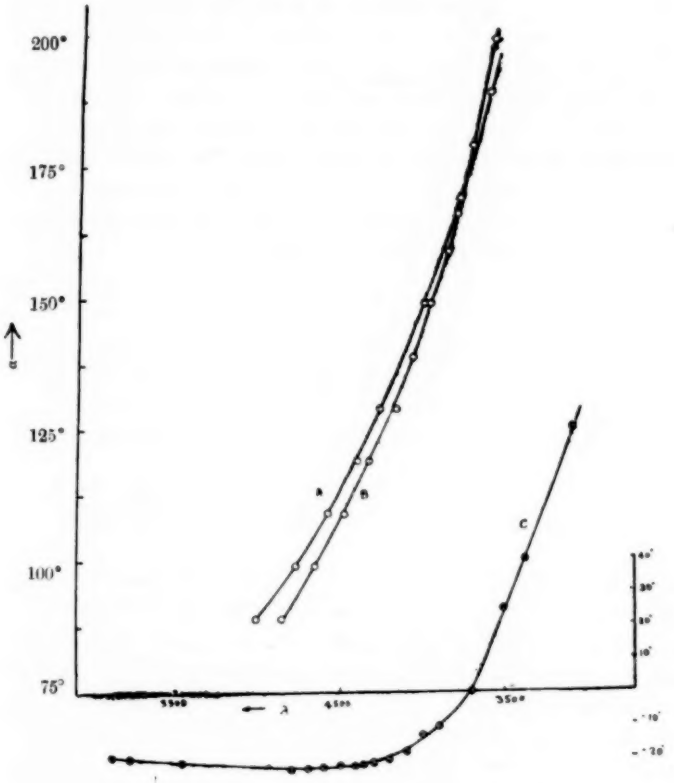
α.	λ with quartz plate alone.	λ with β-pinene & quartz plate.	α.	λ with quartz plate alone.	λ with β-pinene & quartz plate.
88·8	5008	4850	148·8	3955	3919
98·8	4765	4650	158·8	...	3811
108·8	4560	4459	168·8	3732	...
118·8	4380	4310	178·8	...	3652
128·8	4240	4143	188·8	3540	...
138·8	...	4028	198·8	...	3510

In the first and forth columns are given the analyser settings while the second, third, fifth and sixth columns give the corresponding wave-lengths obtained for the quartz plate and for the quartz plate together with the substance under test. From these data the rotatory dispersion curves for the two cases have been drawn and are shown in the Figure 2. C gives the rotatory dispersion curve for β-pinene as calculated from the two curves A and B. It can be seen that the

readings thus obtained lie on a smooth curve with those obtained directly and indicated by crosses on the graph.

FIG. 2.

Rotatory dispersion of β-pinene.



As is shown in detail in a previous communication (Padmabhan and Jatkar, *J. Indian Chem. Soc.*, 1935, **12**, 518) the rotatory dispersion of a pure sample of β-pinene can be expressed satisfactorily by the following two term Drude's equation,

$$[\alpha] = \frac{54{\cdot}7}{\lambda^2 - (0{\cdot}2200)^2} - \frac{63}{\lambda^2 - (0{\cdot}1900)^2}.$$

where $\lambda_1 = 2200$Å represents the first component in the absorption spectrum of β-pinene. This value has been deduced from spectrophotometric measurements of the general absorption of the substance till $\lambda = 2300$Å, on the assumption that a simplified formula of the Ketteler-Helmholtz type

$$\lambda / \sqrt{y} = a\ (\lambda^2 - \lambda_0^2)$$

(where y=optical density and a is a constant) is applicable to the absorption curve (Bruhat, *loc. cit.*). The identity of the second characteristic frequency $\lambda_2 = 1900$Å with that of α-pinene (Padmanabhan and Jatkar, *loc. cit.*) is rendered likely on account of the great structural similarity between the two substances. From the Drude's equation above the optical rotatory power has been calculated for a number of wave-lengths and compared with those obtained by using the modified photographic method as shown below.

TABLE II.

λ	...	5893	5780	5461	4358	3644
$[\alpha]_{abs}$	...	−19·53	−20·04	−21·38	−22·11	−0·8
$[\alpha]_{calc}$	..	−19·1	−19·7	−21·0	−21·8	+0·6
λ	...	5500	5000	4500	4000	3500
$[\alpha]_{abs}$	...	−20·4	−23·0	−22·5	−17·0	+12·0
$[\alpha]_{calc}$	...	−20·8	−22·7	−22·7	−16·4	+12·5

The agreement should be considered satisfactory in view of the small dispersion of the spectrograph used (100Å per mm. at λ4000).

The error involved in such photographic measurements of optical rotatory dispersion depends in general on the accuracy with which the wave-length of equal intensity can be measured and this varies even for the same substance from region to region of the spectrum. If the extinction at λ 4850 in Table I is taken as an example, it was observed that the wave-length of equal intensity can be measured correct to 10Å which corresponds to an error of approximately 0·3 or 1·5% in the measurement of the optical rotation of β-pinene. On the other hand in the photographs obtained with β-pinene alone, there is error of nearly 400Å in the measurement of the wave-length of equal intensity corresponding to an error of approximately one degree or 5% in the optical rotation. It can thus be seen that in spite of the larger magnitude of the rotation, the use of a second substance

ol high dispersive power does help to give a more accurate reading and although it is not claimed that the accuracy obtainable by this method is equal to that of visual observations it seems to be fairly dependable for the measurement in the ultraviolet of substances whose rotatory dispersion is small and for which the usual photographic method does not give accurate results.

Summary.

The usual photographic method for measuring optical rotatory dispersion is not satisfactory for substances whose optical activity does not change very much with wave-length. By determining the rotatory dispersion of such a substance together with another of normal dispersive power and high initial rotation, fairly accurate readings can be obtained. The rotatory dispersion of the latter is then separately determined and by difference the rotatory dispersion of the substance under test can be found out. Readings are given for a particular case β-pinene.

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5-66

Studies in Salt Activation. Part II. Influence of Salts on the Stability of Amylase.

By K. Venkata Giri.

In a previous communication (Giri and Shrikhande, *J. Indian Chem. Soc.*, 1935, **12**, 273) the influence of salts on enzymic hydrolysis of starch has been examined in detail. The conditions under which salts accelerate hydrolysis have been determined. A few points regarding the mechanism of salt activation have also been discussed. It appeared possible that the accelerating effect of salts might be due to the protection of the enzyme against destruction, thereby indirectly accelerating the activity of the enzyme. No quantitative work seems to have been published regarding the stability of amylase in relation to the presence of salts. Hizume (*Biochem. Z.*, 1924, **146**, 52), however, has shown that salivary amylase was protected from heat inactivation by the presence of sodium chloride and other chlorides, by sodium bromide but not by nitrate or iodide. Malt diastase, on the other-hand, was deleteriously affected by the presence of sodium chloride or sodium bromide during heating. In the experiments of Hizume, the p_H of the medium was neither controlled nor observed. Further the influence of salts on the stability of the enzyme was not investigated at varying salt concentrations. The present investigation has shown that the protective action of salts on the enzyme depends on these two factors, *viz.*, the p_H of the medium and the concentration of the salt. By suitably varying these two factors, protection, destruction or no effect on the enzyme can be found. These facts together with the qualitative nature of his results, particularly with malt diastase, indicate that further systematic investigation is necessary. It is interesting in this connection to refer to the work of Sherman and Walker (*J. Amer. Chem. Soc.*, 1923, **45**, 1960) who have shown that the activating action of amino-acids on pancreatic amylase is due in part to a protection of the enzyme from deterioration in the aqueous dispersion in which it acts. The present investigation was undertaken

with a view to know whether neutral salts protect the enzyme from inactivation, and whether there is any relation between the protective action and the accelerating effect of the salts on the enzyme.

Experimental.

The amylase used in the present investigation was prepared from sweet potato and purified by adsorption on alumina gel and elution with phosphate buffer and final dialysis, in the manner described by Giri (*Biochem. Z.*, 1934, **275**, 106). All the salts employed in the present investigation were of the highest grade of purity, either Merck's or Kahlbaum's guaranteed analytical reagents.

The method of measuring the activity of the enzyme was the same as that described in a previous communication (Giri, *J. Indian Chem. Soc.*, 1934, **11**, 338). The reaction mixture (100 c.c.) contained 1 g. of starch, and Walpole's acetate buffer of p_H 6·0, present in a total concentration of 0·04*N*-acetate.

The method of studying the stability of the enzyme was as follows: A series of mixtures containing acetic acid-acetate buffer of known p_H, present in a total concentration of 0·05*N*-acetate, and salt of known concentration were prepared in a series of resistance glass test tubes, the total volume of the mixture amounting to 5 c.c. The tubes containing the mixtures were immersed in a thermostat at 50°. After the temperature of equilibrium was established, 5 c.c. of the enzyme solution were poured into each tube and allowed to remain at the same temperature for 30 minutes. At the end of this period, 5 c.c. of the enzyme mixture were removed from each tube and the activity determined.

The activity is always expressed in terms of the velocity constant *K*. The activity of the enzyme which was kept at room temperature (control) was taken as the standard.

Influence of Salts on the Stability of Amylase at Varying Hydrogen-ion Concentrations.

Enzyme mixtures containing buffer of varying hydrogen-ion concentrations, with and without added salt (NaCl), were prepared. The concentration of NaCl present in the mixture was 0·05*N*. The mixture was kept at 50° for 30 minutes, and the activities determined. The results are given in Table I and graphically represented in Fig. 1.

In the tables V denotes relative reaction velocity and K, the activity.

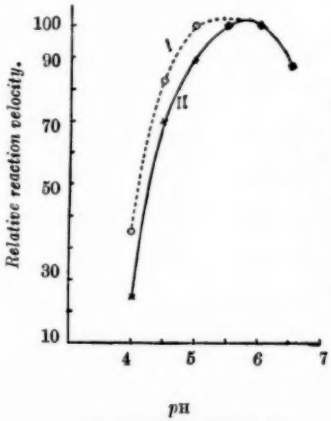
TABLE I.

	Without added salt.		With 0·05N-NaCl.	
p_H.	$K \times 10^4$.	Relative reaction velocity.	$K \times 10^4$.	Relative reaction velocity.
	33·9 (control)	100	33·9 (control)	100
4·0	4·9	14·5	12·0	35·4
4·5	23·7	70·0	28·1	82·9
5·0	30·2	89·0	33·9	100
5·5	33·9	100	33·9	100
6·0	33·9	100	33·9	100
6·5	29·6	87·3	29·6	87·3

It can be seen from Table I that the activity of the enzyme is not changed by keeping it at 50° at p_H 6·0, which is the optimum p_H for the activity of the enzyme. With a view to finding out whether the salt exerts any protective influence on the enzyme at the optimum p_H, the experiment was repeated at 65° and no such effect was observed. Thus the results indicate that the salt protects the enzyme

Fig. 1.

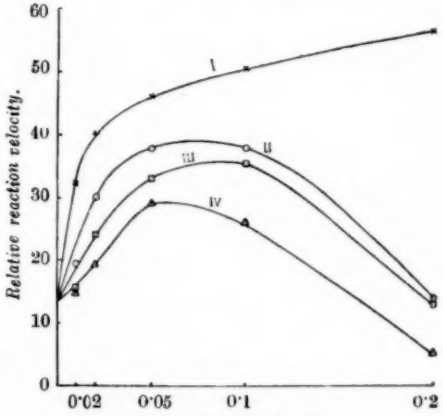
Effect of pH on the stability of amylase.



I—With 0·05N—NaCl.
II—Without added salt.

Fig. 2.

Influence of anion on the stability of amylase



Curves I-IV refer to NaF, NaCl, Na_2SO_4 and $NaNO_3$ respectively.

against destruction at the more acid region of optimum p_H. No such protective effect was observed on the alkaline side of the optimum p_H at the salt concentration investigated. On comparing the curves in Fig. 1 with those obtained in the previous communication (Giri and Shrikhande, *loc. cit.*) which indicate the influence of hydrogen-ion concentration on the accelerating effect of salt, a close similarity on the nature of the curves can be seen. Thus the salt protects the enzyme against destruction at hydrogen-ion concentrations at which it also accelerates the activity of the enzyme.

Influence of the Anion of the Added Salt on the Stability of Amylase.

With a view to ascertain whether the anion of the salt has any influence on the stability of the enzyme similar to that which it has on its activity, experiments were carried out with the fluoride, chloride, sulphate and nitrate of sodium. The composition of the mixture was the same as before, except that the concentration of the salts were varied and the p_H adjusted to 4·0. The results are presented in Table II and in Fig. 2.

TABLE II.

p_H = 4·0. Temperature = 50°.

Salt conc.	NaF		NaCl		Na_2SO_4		$NaNO_3$	
	$K \times 10^4$.	V.	$K \times 10^4$.	V.	$K \times 10^4$.	V.	$K \times 10^4$.	V.
Control	37·3	100	37·3	100	37·3	100	37·3	100
0	4·9	13·2	4·9	13·2	4·9	13·2	4·9	13·2
0·01 *N*	12	32·2	7·3	19·5	5·9	15·8	5·8	15·6
0·02	14·9	40·0	10·8	28·9	8·9	23·8	7·3	19·5
0·05	17·3	46·4	14·1	37·8	12·3	32·9	10·9	28·9
0·10	18·8	50·4	14·1	37·8	13·3	35·6	9·7	26·0
0·20	20·9	56·0	5·3	14·2	5·0	13·4	2·0	5·4

It may be mentioned here that in view of the fact that the fluoride notably displaces the p_H of the buffered enzyme mixtures, the p_H was controlled and checked colorimetrically on an aliquot part of the solution. In this way the possibility of the enzyme solutions being diversely influenced by the difference in p_H was excluded.

The foregoing results show that the stability of the enzyme increases with the salt concentration upto a certain limit and then decreases considerably; sodium fluoride at all concentrations exerts considerable protective influence on the enzyme. Unlike the other salts the protective effect of sodium fluoride does not decrease by further increase in the concentration of the salt. This is consistent with the generally anomalous behaviour of fluorides in relation to other halides. The effectiveness of the salts in protecting the enzyme against destruction can be arranged in the following order: $NaF > NaCl > Na_2SO_4 > NaNO_3$. It will be of interest to note here that in a previous communication on the subject, the accelerating effect of these salts on the activity of the enzyme was found to follow the same order.

Influence of the Cation of the Added Salt on the Stability of Amylase.

The hydrogen-ion concentration was maintained constant as before, and the concentrations of the salts were varied. Table III shows the nature of the results obtained.

TABLE III.

Salt conc.	LiCl		KCl		NaCl		$CaCl_2$	
	$K \times 10^4$.	V.	$K \times 10^4$.	V.	$K \times 10^4$.	V.	$K \times 10^4$.	V.
Control	37·3	100	37·3	100	37·3	100	37·3	100
0	4·9	13·2	4·9	13·2	4·9	13·2	4·9	13·2
0·01*N*	4·9	13·2	4·9	13·2	7·3	19·5	16·2	43·4
0·02	7·6	20·4	8·1	21·7	10·8	28·9	15·9	42·6
0·05	13·3	35·6	13·3	35·6	14·1	37·8	13·7	36·7
0·10	11·5	30·8	12·0	32·1	14·1	37·8	7·3	19·6

The foregoing results would suggest that the protective influence of the salts investigated depends also on the nature of the cation of the salt. Thus $CaCl_2$ at low concentrations protectst he enzyme against destruction, while the other salts require high concentrations to protect it to the same degree. Now considering the possibility that salts accelerate the activity of the enzyme by protecting it against destruction, a similar difference in the cation influence on the

acceleration of the activity of the enzyme is to be expected from these results. But in the previous communication it was found that all the cations had the same accelerating effect on the activity of the enzyme. This discrepancy is easily explained by repeating the experiment at varying concentrations of each salt. The following are the results obtained with varying concentrations of each salt on the activity of the enzyme.

TABLE IV.

Influence of cation on the activity ($K \times 10^4$) *of amylase at* pH 4·0 *and at* 30°.

Salt conc.	LiCl.	KCl.	NaCl.	$CaCl_2$.
0	15·9	15·9	15·9	15·9
0·01*N*	16·6	16·4	17·5	18·0
0·02	17·5	17·5	18·1	22·4
0·05	19·6	19·6	19·8	27·8
0·10	21·4	22·0	23·4	24·5

It can be seen from the results that at low concentrations of the salt the divalent cation Ca has a more accelerating influence on the activity of the enzyme than the monovalent cations. Thus the foregoing results show that there is a parallelism between the influence of the cations on the stability and on the activity of the enzyme.

Influence of Salts on the Stability of Amylase at the Optimum and at the Alkaline side of the Optimum pH.

The experiments were repeated at pH 6·0 (optimum pH) and temperature 65°, and at pH 6·5 and temperature 50°. It was found (Table V) that the salt (NaCl) exerts no influence on the stability of the enzyme, but at high salt concentration (0·1*N*) it renders the enzyme less stable. This is in conformity with a similar behaviour of the salt on the activity of the enzyme. Thus it was shown in a previous communication that sodium chloride does not accelerate the activity of the enzyme at the optimum, and on the alkaline side of the optimum pH; on the contrary, the salt inhibits the activity when its concentration is high.

TABLE V.

Influence of NaCl *on the stability of amylase at* p_H 6·0 *and* 6·5.

NaCl conc. (*N*)	..	0	0·01	0·02	0·05	0·10
$K \times 10^4$. At p_H 6·0	...	2·2	2·2	2·2	2·2	1·9
$K \times 10^4$. At p_H 6·5	...	32·6	32·6	32·6	31·7	27·4

DISCUSSION.

The object of the present investigation was to show whether the salts protect the amylase against destruction and whether there is a parallelism between the influence of these salts on the stability and on the activity of the enzyme. The results show that the conditions favourable for acceleration of the enzyme action are also favourable for the protection of the enzyme against destruction in presence of salts. Thus the salts protect the amylase from destruction at more acid region of the optimum p_H. At the optimum and at the alkaline side of the optimum p_H, they have no influence on the stability of the enzyme; on the contrary they hasten the destruction of the enzyme at high salt concentrations. Under exactly similar conditions, the salts were found to accelerate the activity of the enzyme. Secondly, the order of action of the anions and cations of the salts investigated is similar both for the protection of the enzyme and for the acceleration of the activity of the enzyme. It seems, therefore, reasonable to associate the effects of salts upon the hydrolysis of starch by the enzyme with their influence upon its stability, and to conclude that salts accelerate the activity of the enzyme because they protect it against destruction, and that stronger solutions are inhibitory because they hasten the destruction of the enzyme. It is, however, by no means contended that the protective influence of the salts on the enzyme accounts for the phenomenon of salt action.

SUMMARY.

1. The influence of salts on the stability of amylase from sweet potato has been investigated under varied conditions.

2. The salts protect the enzyme against destruction at more acid region of optimum p_H Individual anions differ very widely in their quantitative influence on the stability of the enzyme. The salts

investigated can be arranged according to the decreasing magnitude of their effect in protecting the enzyme against destruction as follows: $NaF > NaCl > Na_2SO_4 > NaNO_3$. The divalent cation Ca is more efficient than the monovalent cations Li and Na in protecting the enzyme against destruction.

3. An explanation has been advanced for the salt acceleration of the enzymic hydrolysis of starch. The favourable effects of salts at certain concentrations on the hydrolysis of starch by amylase appears to be associated with the increased protection of the enzyme and the inhibitive action at high salt concentrations with decreased stability of the enzyme under these conditions.

The author's thanks are due to Dr. V. Subrahmanyan for his keen interest in the work.

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The Heats of Transition of Triglycerides.

By M. M. Ram Rao and S. K. Kulkarni Jatkar.

The property of exhibiting a double melting point has long been regarded as a characteristic of nearly all triglycerides. Several observers* have recorded that these triglycerides melt at a certain temperature, solidify at one slightly higher, and melt again on further heating.

It will be instructive to compare the "melting points" recorded by Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 155), Löskit (*Z. physikal. Chem.*, 1928, **134**, 137) and Joglekar and Watson (*loc. cit.*). It should be noted that these investigators claim to have purified their specimens with enormous care, Löskit recording 60 crystallisations, while Joglekar proceeded through as many as 40.

* Guth, *Rec. trav. chim.*, 1902, **18**, 169; *cf. Z. Biol.*, 1902, **44**, 78; Grün and Schacht, *Ber.*, 1907, **40**, 1770; *cf. Ber.*, 1912, **45**, 3692; Bömer *Z. Nat. Genussm.*, 1907, **14**, 97; 1909, **16**, 362; Bömer and Limprich, *ibid.*, 1913, **15**, 373; Kremann and Schoulz-Graz, *Monatsh.*, 1912, **33**, 1063; Smits and Bokhorst, *Proc. Acad. Wetensch*, 1913 **15**, 681; Bokhorst, Disseration, Amsterdam, 1916; Nicolet, *Ind. Eng. Chem.*, 1920, **12**, 741; Grün, *Ber.*, 1921, **54B**, 2909; Klimont, *Oest. Chem. Ztg.*, 1922, **25**, 22; Joglekar and Watson, *Chem. und Md.*, 1928, **47**, 365.

TABLE I.

	Laurin.	Myristin.	Palmitin.	Stearin.
I. Stable form.				
(*a*) Joglekar and Watson	46·2	56·5	65·6	71·8
(*b*) Lõskit	46·4	56·5	64·8	71·8
(*c*) Efremov	...	...	67·5	69·3
II. Mittel modification.				
(*b*) Lõskit	...	48·5	55·0	65·4
(*c*) Efremov	...	...	48·4-53·8	53·2-55·2
III. Metastable form.				
(*a*) Joglekar and Watson	18·0	33 0	46·2	55·0
(*b*) Lõskit	36·4	47·0	45·0	55·0
(*c*) Efremov	...	...	48·4	53 2

EXPERIMENTAL.

The present investigation is founded entirely on the following fundamental assumptions:

(1) Triglycerides exist only in two forms.

(2) The metastable solid, obtained on sudden cooling, could be regarded as a pure phase. It will be referred to in this paper as the metastable form.

Heats of Solution of Triglycerides.

If it be granted as exceedingly probable that the glycerides exist in the pure stable form in solution, it would be of interest to measure the heats of the solution of the two forms of each triglyceride in various organic solvents and from the results thus obtained calculate the heat of transition of one form into the other.

To this end in view a twin calorimetric arrangement was set up. The attainment of very high degree of accuracy was never attempted.

The apparatus consisted of two small silvered vacuum flasks similar in size and shape, supported on rubber stoppers on a common wooden mount with a card-board partition between, the whole assemblage slipping into a wooden box. The flasks were closed by stoppers through which passed (*a*) at the centre, a propeller stirrer of glass, (*b*) on one side, away from the neighbouring twin, a heater of Constantan

wire mounted on a glass tube carrying potential and current leads, and (c) on the other side, one arm of an inverted **U**-tube of glass through which one end of a multiple thermel of four junctions passed into the flask.

In one of the twins, a glass tube blown out at lower end into a tiny thin bulb for carrying about 0·2 g. of the substance investigated, was inserted through the stopper. The "dummy" flask was also provided with a similar tube closed at the lower end.

Equal volumes of solvent (50 c.c.) were poured into the twins and the corks replaced. The stirrers were driven by tiny wooden pullies of the same diameter, which were geared on to the pulley of a common motor by a single belt going round all the three. The stirrers were started, and the thermocouple was put on to a sensitive suspended coil-mirror galvanometer. The thermel indicated the difference in temperature between the twins prevailing at any instant to an accuracy of about 0·003°. The galvanometer reading was watched, and when it was steady, it was recorded and the system then could be assumed to be compensated for thermal leakages. The bulb in the one calorimeter was then broken. With the progress of solution the temperature in that calorimeter fell as indicated by the moving spot of light. Heat was simultaneously supplied by the passage of an electric currrent through the heater, until the spot of light was brought back to the zero at start. Being thus a null method, absolute measurements of temperature are not necessary. From the known resistance of the heater, and the potential across it, read on a Weston sub-standard voltmeter included in parallel in the heater circuit, the heat supplied to the calorimeter could be calculated.

The degree of accuracy which this method gives can be seen from the following values obtained for the heat of solution of sodium chloride in water.

TABLE II.

Temp.	Wt. of NaCl. in 50 c.c. H_2O.	Expt. value.	Calc. value(x)	Error.
25·5°	1·0151	991·7 cal./g. mol.	987·9	− 3·9
24·7°	0·9440	1007·8	1008·9	− 1·1
25·8°	1·0220	878·2	879·9	− 1·7

(x calculated from the results of Lipsett, Johnson and Maas, *J. Amer. Chem. Soc.*, 1927, **49**, 1940; taking $\partial H/\partial T = 26{\cdot}4$ cals. per degree.)

TABLE III.

Heat of solution of tristearin.

M. p. 71·4°. Sol. P. = 69·6°

(A) Solvent-toluene.

(a) Form I (stable).			(b) Form II (metastable).		
Wt. in 50 c.c. solvent.	Temp.	Heat of soln.	Wt. in 50 c c. solvent.	Temp.	Heat of soln.
0·191 g.	24·8°	46·85 cal./g.	0·241 g.	25·9°	31·84 cal./g.
0·210	25·2	46 98	0·205	26·5	31·50
0·205	26·2	46·98	0·220	26·9	31·62
		46·98 = 47·00	0·168	26·9	31·64
					31·63 = 32·00

The difference between (*a*) and (*b*) of 15·4 cal. per g. is equal to the heat of transition.

(B) Solvent-carbon tetrachloride.

0 193	25·5	41·82	0·218	25·8	25·8
0·182	26·2	40·61	0·195	25 5	25·4
		41·2			25·6

The difference of 15 6 cal. per g. is equal to the heat of transition.

Better concordance could not be obtained as each time a little substance was left over undissolved.

TABLE IV.

Heat of solution of trilaurine.

M. p. = 65·3°. Sol. p. = 64·3°. Solvent = benzene.

(a) Form I (stable).			(b) Form II (metastable).		
Wt. in 50 c.c. solvent.	Temp.	Heat of soln.	Wt. in 50 c.c. solvent.	Temp.	Heat of soln.
0·159 g.	26·3°	49·49 cal./g.	0·168 g.	26·0°	33·86
0·167	26 5	49·25	0·150	26·5	33·89
		49·33 = 49·3			33·88 = 33·9

The difference of 15·4 cal. per g. is equal to the heat of transition.

The difficulty with laurin is the fact that at laboratory temperature (30°) the metastable solid cannot exist.

So the twin assembly had to be discarded ; one of two flasks was retained, and enclosed in a jacket containing water and the whole was left in a large vacuum flask with ice packing all round. The other junction of thermel was dipping in the jacket water. Where there was a draft observed at the end of the experiment, adequate correction was made for it in the computation of the heat effect.

The new arrangement gave for the heat of solution of NaCl at 30°, 1572 cal. per g. mol., calculated value being 1568 cal.

Heat of solution of trilaurin.

m.p. (stable) 45·8°-46·0°. m. p. (metastable) 18·0°.

TABLE V.

Solvent-toluene.

(*a*) Form I (stable).			(*b*) Form II (metastable).		
Wt. in 50 c.c. solvent.	Temp.	Heat of soln.	Wt. in 50 c.c. solvent.	Temp.	Heat of soln.
0·235 g.	1·2°	37·5	0 274 g.	0·5°	21·9
0·254	1 0	37·4	0·272	1·0	28 2
			0·253	0·0	23·6
		37·5	0·270	0·0	21·4
The values for the metastable form are very discordant.					21·6

The principal difficulty was encountered in the rapid transference in the calorimeter of the metastable substance before it could transform ; and the measurement had to be made in as short a time after insertion of substance into calorimeter as is possible, consistent with the attainment of a uniform common temperature by calorimeter, accessaries and substance. Such attainment was not quite certain since the period that could be permitted for this temperature equalisation could never exceed 15 minutes, after the lapse of which the liability of the metastable solid spontaneously transforming sets in.

It is remarkable that in the case of laurin too, the ' heat of transition ' is in the neighbourhood of 15 cal. per g.

Latent Heats of Fusion.

When the stable from of stearin is heated to its melting point, a liquid is obtained which on sudden cooling gives the metastable solid. Consequently it is reasonable to suppose that stable stearin on melting gives the liquid corresponding to the metastable form; and the same liquid, though at a lower temperature, is obtained on melting the metastable form. If the specific heats of the two forms are not very different, the difference in the latent heats of fusion of the two forms should give the heat of transition of one form into the other.

The aneroid calorimeter has been employed in some very accurate research by Dickinson and Osborne. (*Bull. Bureau of Standards*, 1915, **12**, 23). Using the same design twin aneroids were built with enclosed heaters, and each calorimeter had a narrow re-entrant tube at the centre, closed on top, into which one thermel end could readily slip in. The heater was brought out and connected to terminals fixed to a bakelite base, and they dipped in mercury cups when the calorimeter had been put into the jacket. Between the twins was disposed a bakelite moulded partition carrying on one side a radiation thermel for registering the difference in temperature between calorimeter and jacket. This thermel itself was constructed after the manner described by Miss Wilson and collaborators (*Proc. Phys. Soc.*, 1920, **32**, 326) by winding No. 40 Constantan wire on a glass frame-work and silver plating all the turns on one side of the frame up to the middle of the longer edges, so that along each of these we get a row of 20-30 silver Constantan junctions.

The substance was kept in one of these calorimeters and some liquid paraffin in the other. Both were heated along with the completely enclosing jacket, the heating of the latter being hand controlled. The working calorimeter was heated a little faster than the dummy and the jacket temperature was made to keep pace with the mean of the temperatures of both calorimeter and dummy. The thermel registering the difference in temperature between calorimeter and dummy was put on the galvanometer and the spot of light watched. This will be slowly creeping in some direction. At the melting point, due to absorption of latent heat the dummy will heat up and the movement of the spot will reverse. When the fusion is complete, the working calorimeter will rise quicker in temperature than the dummy as it was doing in the nearly stages. So the spot will again turn back on its course. The exact time between this double reversal

of the movement of the spot of light gives the time of fusion. From the known resistance of the heater and the potential across it, the heat of fusion is readily computed.

The principal difficulty in the manipulation of this apparatus is confined to the hand control of jacket temperature for maintenance of approximately adiabatic conditions. With suitable alterations and the employment of an automatic control of jacket heater it is expected that this method should yield good results.

The accuracy actually attained can be guaged from the following measurements for the latent heat of fusion of palmitic acid : (52·75), 51·59, 51·43, (53·54), 51·65, 51·68 and 51·58, mean 51·6. This value is 0·6 cal. higher than that obtained by Mrs. Stratton and Partington (*Phil. Mag.*, 1922, **43**, 436).

TABLE VI.

The latent heat of fusion of tristearin.

Wt. of substance taken = 2·843 g.

Form I (stable)	... (62·1)	61·6	61·8	61·4	Mean 61·6
From II (metastable)...	44·2	(40·8)	44·2	43·6	Mean 44·2

Eykman gives 45·7.

Since partial transformation takes place during fusion which occupies 20 to 21 minutes, too low a result is obtained for the labile form.

Using Eykman's value in conjunction with the value obtained here for stable form the difference works out as $61·6-45·7=15·9$ cal. for 'heat of transition.'

Tripalmitin gave for the stable form a value of about 62·3 cal. for latent heat. The labile form, however, transforms so quickly that no concordant results for its latent heat of fusion could be obtained.

The above results appear to support the assumption that glycerides exist in stable form in solution. The Raman-effect and *X*-ray diffraction of the two forms of triglycerides are being studied.

SUMMARY.

1. A method employing a double calorimeter has been applied to the determination of the heats of solution of the two modifications of tripalmitin and tristearin in several organic solvents.

2. The difference in the heats of solution of the two forms is constant and equal to the difference in the latent heats, indicating that in

solution these bodies assume the same form (*cf.* Rao and Jatkar, *Proc. Indian Science Congress*, Allahabad, 1930, p. 225).

3. The heats of solution of two forms of triglycerides of trilaurin, tristearin and tripalmitin have been measured by the method of twin calorimeter.

Our thanks are due to Dr. H. E. Watson for his keen interest and guidance during this work.

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Dyes Derived from Acridic Acid.

By Mahadeo Prasad Gupta and Sikhibhushan Dutt.

Acridic acid contains two carboxyl groups in *ortho* positions to one another, and is, therefore, expected to yield dyestuffs on condensation with aromatic amino and hydroxy compounds in the same way as phthalic acid or quinolinic acid (Ghosh, *J. Chem. Soc.*, 1919, **115**, 1102). Recently Tewari and Dutt (*J. Indian Chem. Soc.*, 1928, **5**, 58) have successfully condensed quinoline-1:2:3-tricarboxylic acid with aromatic amino and hydroxy compounds with the production of dyestuffs having interesting properties of colour and fluorescence. They could not condense acridic acid itself on account of the fact that at that time it was practically an inaccessible material, but nevertheless from theoretical considerations they came to the conclusion that dyes derived from acridic acid, even if they could be prepared, would have the same colour as the corresponding dyes derived from quinoline-1:2:3-tricarboxylic acid.

Acridine being now available in quantity, acridic acid was prepared from it by oxidation with potassium permanganate, and the acid condensed with aromatic amino and hydroxy compounds in the usual manner with the production of dyestuffs. When compared with the corresponding dyes derived from quinoline-1:2:3-tricarboxylic acid

it was found that the former class of dyestuffs are much more intensely coloured and far more absorptive than the latter. From this it is quite evident that the extra carboxyl in the dyes derived from quinoline-1:2:3-tricarboxylic acids acts as a bathochrome in reducing the intensity of colour and fluorescence. This fact will be quite apparent from the table of absorption maxima given at the end of the paper.

The following aromatic amino and hydroxy compounds have been condensed with acridic acid and the corresponding dyestuff obtained: phenol, resorcinol, phloroglucinol, hydroxyquinol, *m*-aminophenol, *m*-dimethylaminophenol, *m*-diethylaminophenol, orcinol and *m*-phenylenediamine. The compound with resorcinol has also been brominated and the corresponding tetrabromo derivative obtained. The condensation takes place without the use of any condensing agent, but the addition of a trace of concentrated sulphuric acid is beneficial in producing an increased yield of the dyestuff. In general properties these dyes resemble the corresponding phthaleins, but the intensity of colour is slightly more and the fluorescence slightly less. They dye wool and silk beautiful and brilliant shades.

Experimental.

Preparation of acridic acid.—10 G. of acridine were brought to a fine state of subdivision by solution in dilute hydrochloric acid and precipitation with cold dilute caustic soda. The voluminous precipitate was collected, suspended in water and oxidised with a 2% solution of potassium permanganate. The mixture was heated to boiling and the permanganate added until it was no longer decolourised. The precipitated manganese dioxide was filtered off first through cloth and then through paper, and the filtrate after being neutralised with hydrochloric acid was evaporated to a small volume and allowed to stand when a large amount of potassium chloride crystallised out. The filtrate on acidification with concentrated hydrochloric acid deposited the acridic acid gradually in crystalline crusts which were collected and recrystallised from dilute alcohol in stout prisms, m. p. 128-130° (decomp.).

The condensation of acridic acid with aromatic amino and hydroxy compounds were effected in the same manner as in the case of quinoline-1:2:3-tricarboxylic acid. For the sake of abbreviation, the results are given in tabular forms.

TABLE I

(A = acridien).

Name.	Appearance.	M. p.	Colour in alcohol.	Colour with addition of acid or alkali	Shade on wool or silk.	Analysis Found.	Analysis Req.
Phenol-A	Yellow prisms	184°	Yellow	Crimson (Al)	——	C, 74·26 H, 4·3	74·8 4·06
Resorcinol-A	Brown crystalline powder	203°	Orange-yellow	Orange-red (Al)	Light orange	C 71·82 H, 3·36	72·06 3·89
Phloroglucinol-A	Brown yellow needles	above 280°	Orange-red	Blood-red (Al)	Light tan	N, 3·16	3·38
Hydroxyquinol-A	Brown powder	,, ,,	Brown-red	Violet-red (Al)	Light violet	3·44	3·38
Orcinol-A	Dark brown needles	,, ,,	Orange-yellow	Orange-red (Al)	Light brown	3·15	3·40
m-Aminophenol-A	Yellow-brown prisms	280°-285°	Brown-yellow	Brown-red (Ac)	Light chocolate	10·82	11·02
m-Dimethylamino-phenol-A	Pink needles	168°	Red	Crimson (Ac)	Bright pink	10·13	9·61
m-Diethylamino-phenol-A	,,	120°	Dark-red	Crimson (Ac)	Deep pink	8·26	8·72
m-Phenylenediamine-—A	Brown crusts	295°	Yellow	Orange (Ac)	Chestnut	15·1	14·73
Tetrabromoresorcinol-—A	Bright red prisms	above 290°	Bright pink	Crimson (Al)	Deep pink	Br, 45·22	45·78

TABLE II.

Absorption maxima of the acrideins and analogous dyestuffs.

Name.	-phthalein.	-quinolinein.	-cinchomeronein.	-quinoline 1 :2 :3-tricarboxylein.	-acridien.
Phenol-	5540Å	5560Å	5520Å	5560Å	5880Å
Resorcinol-	4940	4950	4950	4930	5000
Phloroglucinol-	4980	4990	4980	4930	5055
m-Diethylaminophenol-	5510	5540	5540	5540	5930
Tetrabromoresorcinol-	5250	5250	5250	5180	5460

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A New Volumetric Method for the Estimation of Lead.

BY SACHINDRA NATH ROY.

Various methods have been proposed by different investigators for estimating lead volumetrically, the dichromate method being perhaps the most convenient. The object of the present paper is to describe a very simple and ready method for the estimation of lead volumetrically, in the absence of other metallic ions. It was found that neutral solutions of lead can be titrated with standard potassium sulphate solution, the end-point being determined by the use of fluoroscein as an external indicator. In the concentrated solutions the end-point is quite sharp, the indicator (greenish-yellow) becoming vermilion-red in presence of Pb-ions. In dilute solutions the change in the colour of the indicator is not so sharp. With the decrease of the concentration of Pb ions, the red colour gradually fades to a distinct yellow, which persists so long as Pb-ions are present.

Acid solutions of lead should be evaporated to dryness on a water-bath and the slight hydrolysis which might take place will not affect the result, as the solubility product of lead sulphate is much below that of the basic salt formed. The acid solutions cannot be

neutralised with ammonia as the presence of ammonium salts was found to affect the colour reaction with fluoroscein. The evaporated solid is next extracted with minimum quantity of water (perferably 30 to 40 c.c.) and transferred to a conical flask. 5-10 C.c. of rectified spirit are added to the solution, which is then titrated with standard potassium sulphate solution. Small drops of the indicator (0·2% solution of sodium fluoroscinate in water) are placed on a white glazed porcelain tile and drops from the solution of lead are brought and touched with the indicator, the end-point being obtained when there is no change in the colouration of the indicator. A blank experiment may with advantage be performed by touching a similar droplet of the indicator with a drop of water for the final comparison.

This method also appears suitable for the estimation of sulphate by adding to the solution of the sulphate an excess of a standard solution of lead and titrating the excess of lead with standard potassium sulphate.

The yellow colour which gives the indication of the presence of lead persists so long as there is 0·03 to 0·02 mg. of lead per c.c. Inspite of the limited applicability of the method, the results obtained with fairly concentrated solutions (1 to 3%) of lead, is quite satisfactory. The results are given in the following table.

Approx. conc. of soln.	Wt. of the Pb as found in a given vol. by direct estimation as $PbSO_4$.	Wt. of Pb as $PbSO_4$ in the same vol. by the given method.	% Error.
0·50 *N*	1·9790	1·9850	+0·30
0·35	1·0220	1·0180	−0·39
0·20	0·6292	0·6320	+0·44
0·15	0·5134	0·5108	−0·50
0·10	0·3954	0·3967	+0·30
0·075	0·2570	0·2556	−0·54
0 05	0·1985	0·1976	−0·46

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Chemical Examination of *Cuscuta Reflexa*, Roxb. Part II. The Constitution of Cuscutalin.

By Radha Raman Agarwal and Sikhibhushan Dutt.

In a previous communication Agarwal and Dutt (*J. Indian Chem. Soc.*, 1935, **12**, 384) in the course of their investigations on the chemical constituents of *Cuscuta reflexa*, Roxb. (Syn. Amerbel) of the Natural Order *Convulvulaceae*, isolated from it a white crystalline substance of the nature of a lactone called by them cuscutalin (about 1·5%). In the present paper it is proposed to throw some light on the chemical constitution of the aforesaid cuscutalin.

The elementary analysis and the molecular weight determination established the formula $C_{18}H_{10}O_4$. Out of the four oxygen atoms one is present as a phenolic hydroxy group, since it forms a mono-acetyl and a monocarbethoxy derivative. It also gave a light red colouration with alcoholic ferric chloride, but no precipitate with lead acetate, silver nitrate or mercuric chloride.

Although containing no aldehydic or ketonic groups, since it does not react with hydroxylamine, phenylhydrazine, semicarbazide, nor reduces Fehling's solution, cuscutalin reduces Tollen's reagent gradually. An alcoholic solution of cuscutalin could also be slowly titrated with alkalis. It dissolves in alcoholic caustic potash on warming with a beautiful yellow colouration and gives a reddish brown colour with alkaline potassium nitroprusside. These reactions place it beyond doubt into the group of $\triangle^{\alpha\beta}$-unsaturated lactones which were first of all studied by Thiele (*Annalen*, 1901, **319**, 155) and more exhaustively by Jacobs and collaborators (*J. Biol. Chem.*, 1926, **67**, 333; *Phys. Rev.*, 1933, **13**, 222). Jacobs (*loc. cit.*) got so uniform results with all the $\triangle^{\alpha\beta}$-and $\triangle^{\beta\gamma}$-lactones in the light of the reactions enumerated by Thiele (*loc. cit.*) that there appears to be complete justification in considering this substance to be $\triangle^{\alpha\beta}$-unsaturated lactone. From some of the Indian medicinal plants also, substances of the nature of lactone have been isolated and they have without fail given all the reactions of Thiele (*loc. cit.*). Sen (*J. Indian Chem. Soc.*, 1931, **8**, 651) isolated corchoritin from jute seeds, Dikshit and Dutt (*J. Indian Chem. Soc.*, 1930, **7**, 759) marmelosin from *Aegle marmelos* and Agarwal and Dutt (*Current Science*, 1934, **3**, 250; *Proc. Acad. Sci.*

U. P., 1935, **3**, 250) α-elaterin from *Citrullus colocynthis* which were all unsaturated lactones and gave reactions described above. Thus out of the four oxygen atoms, three have been accounted for, one in the hydroxy group and two in the lactonic grouping. On complete methylation with methyl sulphate after first saponifying the lactone with caustic potash, a dimethoxymonomethyl ester was obtained. This was evidently due to the breaking of the lactone by saponification and subsequent methylation.

Cuscutalin is unsaturated. It decolourises bromine water slowly and bromine in chloroform readily. It also decolourises an alkaline solution of potassium permanganate quite easily. On treatment with bromine in chloroform a dibromo-bromide was obtained, containing three atoms of bromine and also one unsaturated linkage. It could also be reduced by zinc dust and acetic acid to give a dihydro derivative. Volumetric estimation of unsaturation in the usual manner established the presence of two double bonds in the molecule. The tetrabromo derivative could not be prepared in a crystalline state.

Cuscutalin being a hydroxy lactone was easily acted upon by concentrated hydrochloric acid to form anhydrocuscutalin. By this reaction the hydroxy group was lost since anhydrocuscutalin gave no acetyl derivative.

Cuscutalin dissolves in boiling alcoholic potash with frothing and on acidification liberated the lactone of another isomeric acid melting at 103° and possessing the same empirical formula as cuscutalin. The acid could not be isolated as such. Cuscutalin is optically active and in chloroform gave a small *dextro* rotation of $[\alpha]_D^{27°} = +8°$.

On fusion with caustic potash cuscutalin gave formic acid, cinnamic acid and an aromatic unsaturated hydrocarbon, (m.p. 82°), which could not be identified. On oxidation with a 3% alkaline solution of potassium permanganate, oxalic acid and benzaldehyde were detected. The formation of benzaldehyde may be due to the oxidation of cinnamic acid which might have been formed as an intermediate product. On heating carefully by itself in a dry tube, cuscutalin first melts, then carbonises and partially sublimes unchanged. A small amount of the anhydrocuscutalin was also detected along with some unidentified hydrocarbons in the process of dry distillation.

Experimental.

The crude cuscutalin ($C_{18}H_{10}O_4$) can be crystallised first from methyl alcohol which leaves a brown waxy matter, and finally from

ethyl alcohol whereby colourless flakes of cuscutalin are obtained melting sharp at 68°.

Monoacetylcuscutalin.—1 G. of cuscutalin was refluxed on a sand-bath with excess of acetic anhydride (25 c. c.) and fused sodium acetate for about 2 hours. An oil separated which solidified to a greyish white amorphous mass on pouring the mixture into water. It was collected, dried and dissolved in hot methyl alcohol. A portion (m.p. 60-62°) remained undissolved and the methyl alcoholic solution on concentration and standing deposited the acetyl derivative in fine colourless plates, m.p. 74°. (Found: C, 72·0; H, 3·9. $C_{20}H_{12}O_5$ requires C, 72·3; H, 3·6 per cent).

Monocarbethoxy-cuscutalin.—Ethyl chloroformate was added drop by drop till in excess to 1 g. of cuscutalin suspended in pyridine. The mixture was then rapidly shaken whereby a pink coloured solution was obtained. After about half an hour of vigorous shaking the solution was poured into water when it separated in thin colourless form. It was kept overnight, filtered and dried. The crude product melted at 80° but on crystallisation from alcohol, from which colourless flakes were obtained, it melted at 105°. (Found: C, 70·0; H, 4·1. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·8 per cent).

Dimethoxycuscutalin monomethyl ester.—Cuscutalin (0·8 g.) was saponified by warming with caustic potash (10 %, 25 c.c.) and the yellow solution treated drop by drop with the theoretical quantity of dimethylsulphate with vigorous shaking. After about 4 hours of shaking the ester separated as an oil on the top, which on keeping with water overnight solidified. This was collected, powdered and crystallised from ethyl alcohol as white microcrystalline substance, m p. 78°. (Found: C, 71·4; H, 5·2. $C_{21}H_{18}O_5$ requires C, 71·99; H, 5·14 per cent).

Anhydrocuscutalin.—Cuscutalin (1 g.) was dissolved by slight warming in concentrated hydrochloric acid (sp. gr. 1·19, 25 c.c.) and the light yellow solution was then heated for about half an hour. Some crystalline suspension began to separate and on cooling the solution the anhydro derivative separated in an amorphous form. It was filtered, washed thoroughly with hot water until free from acid and finally dried over caustic potash. The vitreous mass was then crystallised from hot ethyl alcohol as fine colourless needles, m.p. 71-72°. (Found: C, 79·1; H, 3·00. $C_{18}H_8O_3$ requires C, 79·41; H, 2·94 per cent).

Dibromocuscutalin bromide.—Cuscutalin (1·3 g.) dissolved in chloroform (100 c.c.) was treated with an excess of bromine (3 c.c.) dissolved in chloroform. The mixture was placed in a dark place for some time. It was then refluxed over a water-bath, when fumes of hydrogen bromide were given off. The excess of bromine and chloroform were then removed and the product on being dried over quicklime for about a week solidified to a dark coloured amorphous mass. It was finally crystallised from dilute acetic acid as pale brownish yellow microcrystalline powder, m.p. 64°. (Found: Br, 45·1. $C_{18}H_9O_4Br_3$ requires Br, 45·36 per cent).

The volumetric estimation of unsaturation in cuscutalin (0·43 g.) dissolved in carbon tetrachloride (10 c.c.) was carried out in the usual way. It showed two double bonds in the molecule.

Dihydrocuscutalin.—Cuscutalin (1 g.) was dissolved in hot glacial acetic acid (50 c.c.) and the solution treated with zinc dust (10 g.) in small quantities. When the reaction was complete, the mixture was filtered hot into a large volume of cold water. The reduced product separated as a fine colourless precipitate, which was crystallised from alcohol in fine white flakes, m p. 91°. (Found: C, 73·69; H, 4·50. $C_{18}H_{12}O_4$ requires C, 73·99; H, 4·11 per cent).

Neutralisation value of cuscutalin.—Titration of cuscutalin with standard alkali was possible and the neutralisation value was found to be 17·8, the neutralisation equivalent is 266. The *saponification value of cuscutalin*, determined in the usual manner, was 321·8 and the saponification equivalent 173·9.

Action of alcoholic potash on cuscutalin.—Cuscutalin (5 g.) was saponified by boiling with 0·1 *N*-alcoholic potash. When the saponification was complete the brilliant yellow solution was cooled and the alcohol removed. The mass was then acidified with acetic acid, when a voluminous flocculent mass separated, which was collected and crystallised from alcohol as colourless scales, m.p. 102°. It dissolved in ethyl alcohol, methyl alcohol and acetic acid slowly. It developed a pinkish red colouration with concentrated sulphuric acid on warming. (Found: C, 74·1; H, 3·9. $C_{18}H_{10}O_4$ requires C, 74·5; H, 3·4 per cent).

Caustic potash fusion of cuscutalin.—Cuscutalin (5 g.) was heated with solid caustic potash (50 g.) moistened with a little water (5 c.c.) in a nickel crucible at 140-150° for about 2 hours and then at 180° for 1 hour. The melt boiled with considerable frothing at first and the smell of formic acid was evolved. The dirty white melt was

cooled and lixiviated with water when a white substance remained undissolved. The solution was concentrated, acidified with a little hydrochloric acid and extracted repeatedly with ether, the ether removed when an acid was obtained as fine shining needles, m.p. 132°. It was partly soluble in water, insoluble in petroleum ether and could be crystallised from alcohol in large needles. It gave a very faint colour with ferric chloride. A dilute solution of potassium permanganate and bromine water were decolourised. The analysis of its lead salt gave, taking it to be monobasic, M.W. 142. This was identified to be cinnamic acid. The mother liquor on examination gave tests for formic acid.

The alkali-insoluble portion was dried and refluxed with methyl alcohol, when a portion, greyish white in appearance (m.p. 64°), remained undissolved. The soluble portion on cooling deposited colourless flakes, m.p. 80-84°, suspected to be some aromatic unsaturated hydrocarbon. A solution of potassium permanganate and bromine water were decolourised; concentrated sulphuric acid had no reaction. The yield obtained was too poor to admit of any detailed investigation.

Oxidation of cuscutalin with potassium permanganate.—Cuscutalin (3 g.) in dilute caustic soda solution was treated on the water-bath with an aqueous solution of potassium permanganate (3%) in a big porcelain basin; smell of benzaldehyde was detected in the process of oxidation. The solution of permanganate was decolourised and manganese dioxide was filtered off and the filtrate evaporated to a small volume. On acidification and extraction with ether traces of oxalic acid were detected and confirmed by preparation of the calcium salt.

Action of heat on cuscutalin.—Cuscutalin (3 g.) was very gradually heated in a small distilling flask. It first melted to a colourless liquid which gradually became brown and evolved white fumes which were collected in a test tube containing a little water. A small quantity of unidentifiable products was obtained. From the sides of the flask a substance was obtained, m.p. 71-72°, which was identified as anhydrocuscutalin. No other product could be separated.

One of us (R.R.A.) wishes to express his indebtedness to the 'Kanta Prasad Trust' of the Allahabad University for a research scholarship which enabled him to investigate this problem.

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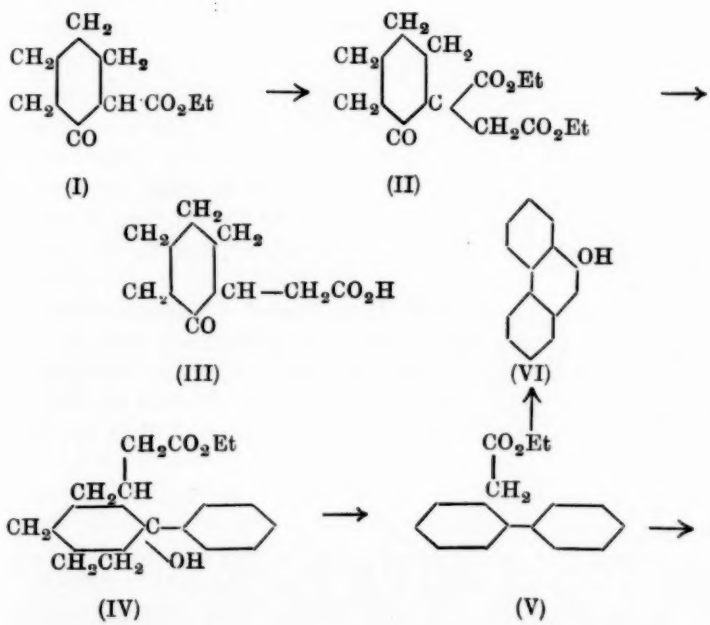
Studies in Diphenyl Series. Part III. A New Route to Phenanthrene.

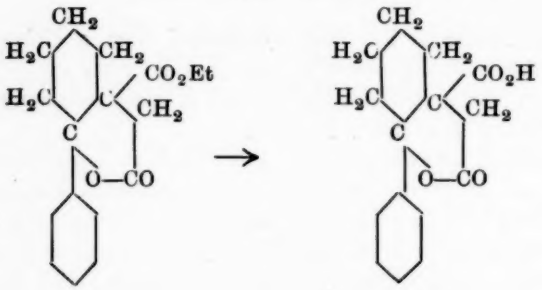
By Nripendra Nath Chatterjee.

9-Hydroxyphenanthrene has been synthesised from a diphenyl derivative and this method seems to be more general for the synthesis of phenanthrenes than the method outlined in a previous communication (*J. Indian Chem. Soc.*, 1935, **12**, 418).

Ethyl *cyclo*hexanone-2-carboxylate (I) is condensed with ethyl chloroacetate and the diethyl *cyclo*hexanone-2-carboxylate-2-acetate (II), thus obtained, is hydrolysed to yield *cyclo*hexanone-2-acetic acid (III). After esterification it is treated with phenyl magnesium bromide and the ethyl 1-hydroxyhexahydrodiphenyl-2-acetate (IV), thus obtained, is dehydrogenated by means of sulphur when ethyl diphenyl-2-acetate (V) is obtained. Ethyl diphenyl-2-acetate after hydrolysis is treated with sulphuric acid when 9-hydroxy-phenanthrene (VI) is obtained. Phenanthrene can be obtained from it by heating with selenium.



Ethyl 1-hydroxyhexahydrodiphenyl-2-acetate gives the corresponding acid on hydrolysis. The compound (II), when submitted to Grignard's reaction, gives a lactone (VII) which on hydrolysis with caustic potash gives the lactonic acid (VIII).



(VII) (VIII)

This lactone may also be utilised for the synthesis of phenanthrene. Further work is in progress.

Experimental.

Diethyl cyclo*hexanone*-2-*carboxylate*-2-*acetate* (II).—Ethyl *cyclo*hexanone-2-carboxylate (25 g.) was added to a solution of sodium (3·4 g.) in alcohol (31 c.c.) and the solid sodium salt was heated under reflux for 6 hours with ethyl chloroacetate (19 g.). After dilution the condensation product was extracted with ether, the ether removed and the product distilled at 168°-175°/11 mm ; yield 18 g. (Found: C, 60·6 ; H, 7·7. $C_{13}H_{20}O_5$ requires C, 60·9 ; H, 7·8 per cent).

cyclo*Hexanone*-2-*acetic acid* (III).—Diethyl *cyclo*hexanone-2-carboxylate-2-acetate (20 g.) was boiled with concentrated hydrochloric acid (2 vol.) for 7 hours. After removal of the mineral acid under reduced pressure, *cyclo*hexanone-2-acetic acid was distilled at 163°/4 mm. (Found: C, 61·2; H, 7·5. $C_8H_{12}O_3$ requires C, 61·5; H, 7·6 per cent).

Ethyl cyclo*hexanone*-2-*acetate* was obtained by esterifying *cyclo*hexanone-2-acetic acid with 3 parts of alcohol saturated at 0° with hydrochloric acid at room temperature and keeping overnight. It was isolated as usual and distilled at 122°/5 mm. (Found: C, 65·0; H, 8·5. $C_{10}H_{16}O_3$ requires C, 65·1; H, 8·6 per cent). The *semicarba-*

zone crystallised from alcohol, m.p. 196-97°. (Found: N, 17·8. $C_{11}H_{19}O_3N_3$ requires N, 17·4 per cent).

Ethyl 1-*hydroxyhexahydrodiphenyl*-2-*acetate* (IV).—Phenyl magnesium bromide (from 2·3 c.c. of bromobenzene and 0·82 g. of magnesium) was added drop by drop to a cooled ethereal solution of *cyclo*hexanone-2-acetate (4 g.) and the mixture left overnight. The product was decomposed with dilute sulphuric acid, the ether removed and it was distilled at 170-180°/8 mm. (Found: C, 73·0; H, 8·1. $C_{16}H_{22}O_3$ requires C, 73·2; H, 8·3 per cent).

1-*Hydroxyhexahydrodiphenyl*-2-*acetic acid* was obtained on refluxing ethyl 1-hydroxyhexahydrodiphenyl-2-acetate with alcoholic potash for 2 hours. The alcohol was distilled off and after dilution the unchanged ester was removed by ether. The aqueous layer was concentrated and after acidification the free acid was extracted with ether, the ether removed, the product kept in a vacuum desiccator for 2 days when it solidified. It was finally crystallised from water, m.p. 129°. (Found: C, 71·6; H, 7·5. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·6 per cent).

Diethyl 1-*hydroxyhexahydrodiphenyl*-2-*acetate*-2-*carboxylate* and *its lactone* (VII).—When an ethereal solution of diethyl *cyclo*hexanone-2-carboxylate-2-acetate was treated with phenyl magnesium bromide a gelatinous precipitate separated. The mixture was left overnight and decomposed with dilute sulphuric acid, extracted with ether, the product collecting at 180°-190°/9 mm. was found to be a liquid while that coming between 190°-220°/9 mm. was found to solidify at the laboratory temperature. From the second fraction, the solid was obtained in a pure form by crystallising from alcohol, m.p. 97°, and it was found to be the lactone of diethyl 1-hydroxyhexahydrodiphenyl-2-acetate-2-carboxylate. (Found: C, 70·9; H, 6·9. $C_{17}H_{20}O_4$ requires C, 70·8; H, 6·9 per cent).

It is possible to convert the liquid (b.p. 180-190°/9 mm.), which is diethyl 1-hydroxy-hexahydrodiphenyl-2-acetate-2-carboxylate into the solid, by leaving it in a desiccator over H_2SO_4 for several days. (Found: C, 68·4; H, 7·9. $C_{19}H_{26}O_5$ requires C, 68·2; H, 7·7 per cent).

The *lactone* of 1-*hydroxy-hexahydrodiphenyl*-2-*carboxy*-2-*acetic acid* (VIII) was obtained by hydrolysing the ester by refluxing with alcoholic potash for 3 hours. After removing the alcohol it was diluted and the ester removed by ether. The aqueous layer was concentrated, acidified and extracted with ether, the ether removed

and the product was kept in a desiccator for 2 days when it solidified. It was crystallised from water, m.p. 141°. (Found: C, 69·0; H, 6·0. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·1 per cent).

Ethyl diphenyl-2-acetate (V).—Ethyl 1-hydroxyhexahydrodiphenyl-2-acetate was dehydrogenated by means of sulphur and the product after washing with caustic alkali was distilled at 165-175°/8 mm. (Found: C, 79·7; H, 6·2. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·6 per cent).

9-*Hydroxyphenanthrene* (VI).—Ethyl diphenyl-2-acetate was hydrolysed by means of alcoholic potash and the product was heated with concentrated sulphuric acid on the water-bath for some time. After dilution it was distilled in vacuum and the portion coming between 220-260°/12 mm. was dissolved in alcohol, and a saturated solution of picric acid added, when a red-coloured picrate was precipitated. It was filtered, washed and recrystallised from alcohol, m.p. 185°. 9-Hydroxyphenanthrene, regenerated from the pure picrate, melts at 153°.

In conclusion the author desires to express his thanks to Prof. Dr. P. C. Mitter for encouragement and advice during the course of this work.

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The Action of Hydrogen Sulphide on the Chromates of Hydrogen, Ammonium, Sodium and Potassium.

By M. A. Hamid, Gurcharan Singh and H. B. Dunnicliff.

This work continues the investigation of the reducing action of hydrogen sulphide on potassium and sodium chromates (Dunnicliff and Soni, *J. Phys. Chem.*, 1929, **33**, 81), chromic acid (Dunnicliff and Kotwani, *ibid.*, 1931, **35**, 3214) and potassium and sodium dichromate (Kotwani, Hamid and Dunnicliff, *ibid.*, 1935, in the Press.)

Dunnicliff and Prakash (*J. Indian Chem. Soc.*, 1935, **12**, 505) have shown that, in certain circumstances, sulphite is formed in the precipitate and this confirms Dunnicliff and his co-workers in the view that sulphite is the precursor of both sulphate and thiosulphate in this series of reactions.

It appears that oxygen (as chromic acid) and sulphur compete for the sulphite and that the proportions of thiosulphate and sulphate vary according to the conditions of the reaction, the sulphate being apparently completely suppressed in the presence of much alkali while both radicals appear when chromic acid is reduced.

Sulphite has never been detected in the reduction of hydrogen, ammonium, sodium or potassium chromates at any temperature whatever the concentration, even when air was very carefully excluded. All the work in the last paper (Y. S. potassium dichromate) was carried out at 19-20°. It is clear that if, by any chance, the reaction $(SO_3)'' + O \longrightarrow (SO_4)''$ is more accelerated at higher temperatures than the reaction $(SO_3)'' + S \longrightarrow (S_2O_3)''$, sulphate might appear, even though only in small quantities, in the end-products.

Sulphate has never been detected among the reduction products of ammonium, sodium or potassium chromates at any temperature or concentration but, when ammonium or potassium dichromate was treated with hydrogen sulphide at 90-95°, air being carefully excluded, sulphate made its appearance. The results using methods of analysis and calculation previously described are shown in Table I.

TABLE I.

		Filtrate		Precipitate			Total	Total	Total
		(S_2O_3).	(SO_4).	(S_2O_3)	(SO_4).	S.	(S_2O_3).	(SO_4).	Cr_2O_7.
$K_2Cr_2O_7$	1.	9·96 g.	1·65 g.	1·90 g.	0·62 g.	16·55 g.	11·86 g.	2·27 g.	
						50·69*	41·50*	9·27*	101·46%
	2.	10·26	1·59	1·86	0·65	16·14	12·12	2·24	
						49·42*	42·42*	9·14*	100·98
$(NH_4)_2Cr_2O_7$	1.	9·74	2·54	2·56	1·12	19·85	12·30	3·66	
						52·11†	36·90†	12·81†	101·82
	2.	10·12	2·48	2·38	1·26	19·54	12·50	3·74	
						51·20†	37·50†	13·09†	101·79

* In terms of $K_2Cr_2O_7$. † In terms of $(NH_4)_2Cr_2O_7$.

These results suggest that a rise of temperature favours the formation of sulphate at the expense of thiosulphate. If this is so, the reduction of chromic acid at high temperatures should show an increase of sulphate at the expense of thiosulphate.

Comparative values found for reduction of chromic acid at 90-95° and at 20° are shown in Table II.

TABLE II.

				In terms of CrO_3			
	(S_2O_3)	(SO_4)	Free S.	S_2O_3.	SO_4.	S.	Total.
		At 90-95°.					
1.	1·08 g.	27·24 g.	10·38 g.	2·56	75·66	21·62	99·84
2.	1·12	27·14	10·26	2·66	75·39	21·38	99·43
		At 20°.					
3.	5·96	25·22	7·30	14·17	70·06	15·21	99·44

When hydrogen sulphide was passed through 50 c. c. of 5% $K_2Cr_2O_7$ at 90-95° for different intervals of time and the sulphate determined in the precipitates, it was shown that, when the brownish colour due to chromium dioxide has disappeared, no more sulphate is formed and the filtrate is alkaline. Duplicate results are shown in Table III.

TABLE III

Time (approx.).	Colour and reaction.	I		II	
		$BaSO_4$.	(SO_4) calc.	$BaSO_4$.	(SO_4) calc.
5 min.	Brown, acidic	0·0228 g.	0·0094 g.	0·0206 g.	0·0085 g.
10	Brownish green, almost neutral	0·0362	0·0149	0·0334	0·0138
15	Green, alkaline	0·0366	0·0146	0·0362	0·0149
30	Green, alkaline	0·0366	0·0151	0·0356	0·0146

These results confirm the view that the formation of sulphate is suppresed by an alkaline medium.

The Action of Hydrogen Sulphide on Ammonium Chromate and Dichromate.

When ammonium dichromate was treated at ordinary temperatures in exactly the method described for potassium dichromate (*loc. cit.*), the filtrates presented no new feature of interest but the intermediate brown precipitate contained chromium dioxide and hydroxide, thiosulphate, one or more thionates, sulphide, ammonium, ammonia (adsorbed and co-ordinated) and free sulphur.

The final green precipitate contained chromium hydroxide, thiosulphate, sulphide, ammonia (adsorbed and co-ordinated) and free sulphur.

Part of the ammonia is removable by continued washing with warm water but the rest is not expelled until the precipitate is heated with concentrated potash. Similarly, sulphide cannot be completely removed by washing, the final residue requiring treatment with acid for complete elimination of sulphide.

Table IV, condensed from a much larger number of analyses, indicates a sudden rise in ammonia (columus 3+4) at No 6 and sulphide at No. 4, which suggests ammine formation in the first case and, in the other, a compound containing co-ordinated hydrogen sulphide molecules—a new feature of particular interest although these chromium compounds are not capable of identification in so complicated a mixture.

TABLE IV.

Estimation of ammonia and sulphide.

Values correspond to 1 g. of ammonium dichromate.

No.	Vol. of H_2S-water used.	Co-ord. sulphide in ppt.	Co-ord. NH_3 in ppt.	NH_3 in filtrate.	Total NH_3 (Theory = 0·1349 g.).
1	30 c. c.	Absent	0·0063	0·1286	0·1349
2	50	Absent	0·0060	0·1280	0·1340
3	70	0·0032	0·0062	0·1271	0·1333
4	90	0·0032	0·0116	0·1220	0·1336
5	110	0·0072	0·0116	0·1230	0·1346
6	170	0·0307	0·0119	0·1229	0·1348
7	210	0·0313	0·0116	0·1218	0·1334
8	250	0·0492	0·0118	0·1216	0·1334

The reaction has to be carried out with full precautions against the loss of ammonia, of which both the filtrate and the precipitate smell strongly. The values in the last column show that this has been achieved.

Table V*a* shows the values for components in the filtrate with increasing amounts of aqueous hydrogen sulphide and Table V*b*, the corresponding analyses for the precipitates at each stage.

TABLE V*a*.

Filtrate.

Values are shown for 1 g. of ammonium dichromate.

No.	Colour and reaction.	Vol. of H_2S soln. used.	CrO_4 in terms of $(NH_4)_2Cr_2O_7$.	Thionate in terms of SO_4.	Thiosulphate (S_2O_3).
1	Brown, acid	30 c.c.	0·6353 g.	0·0677 g.	0·0251 g.
2	Brown, neutral	40	0·5060	0·1179	0·0584
3	Light green, alkaline	50	0·3150	0·1419	0·0769
4	,, ,,	60	0·3037	0·1437	0·0917
5	,, ,,	70	0·2633	0·1422	0·1004
6	,, ,,	80	0·2284	0·1179	0·0892
7	,, ,,	90	0·1286	0·1075	0·0832
8	,, ,,	100	0·1254	0·0548	0·0776
9	Green, alkaline	110	0·1246	0·0540	0·0749
10	,, ,,	130	0·1196	0·0530	0·0567
11	,, ,,	150	0·1063	0·0141	0·0505
12	,, ,,	170	0·0643	0·0084	0·0482
13	,, ,,	190	Absent	Absent	0·0391
14	,, ,,	210	,,	,,	0·0371

TABLE V*b*.

Precipitate.

Values are shown for 1 g. of ammonium dichromate.

Expt. No.	Chromate in terms of $(NH_4)_2Cr_2O_7$.	Cr_2O_3.	Corresponding $(NH_4)_2Cr_2O_7$.	Thionate in terms of (SO_4).	(S_2O_3).	$(NH_4)_2Cr_2O_7$ in the ppt.
1	0·0822 g.	0·1560 g.	0·2586 g.	0·0107 g.	0·0371 g.	0·3408 g.
2	0·0863	0·2472	0·3898	0·0387	0·0860	0·4760
3	0·1224	0·3092	0·5126	0·0314	0·0923	0·6350
4	0·1048	0·3418	0·5667	0·0302	0·1001	0·6715
5	0·0746	0·3862	0·6404	0·0193	0·1094	0·7150
6	0·0722	0·4061	0·4738	0·0135	0·1084	0·7460
7	0·0684	0·4762	0·7893	0·0101	0·1092	0·8577
8	0·0426	0·4929	0·8167	0·0063	0·1083	0·8593
9	0·0184	0·5023	0·8328	0·0064	0·1074	0·8512
10	Absent	0·5224	0·8661	Absent	0·1054	0·8661
11	,,	0·5286	0·8764	,,	0·1044	0·8764
12	,,	0·5246	0·9264	,,	0·1026	0·9264
13	,,	0·6022	0·9984	,,	0·1103	0·9984
14	,,	0·6013	0·9969	,,	0·1109	0·9969

TABLE V*c*.

Expt. No.	Total $(NH_4)_2Cr_2O_7$ in ppt. & filtrate.	Total tetrathionate in terms of SO_4 in ppt. & filtrate.	Total S_2O_3 in ppt. & filtrate.	Expt. No.	Total $(NH_4)_2Cr_2O_7$ in ppt. & filtrate.	Total tetrathionate in terms of SO_4 in ppt. & filtrate.	Total S_2O_3 in ppt. & filtrate.
1	0·9761 g	0·1084 g.	0·0622 g.	8	0·9847 g.	0·0611 g.	0·1859 g.
2	0·9820	0·1566	0·1444	9	0·9758	0·0604	0·1823
3	0·9801	0·1733	0·1692	10	0·9857	0·0530	0·1621
4	0·9752	0·1739	0·1918	11	0·9827	0·0141	0·1549
5	0·9783	0·1615	0·2098	12	0·9907	0·0084	0·1508
6	0·9744	0·1314	0·1976	13	0·9984	Absent	0·1494
7	0·9863	0·1176	0·1924	14	0·9969	,,	0·1480

Table Vc shows that tetrathionate, formed in the side reaction,

$$2\,(NH_4)_2S_2O_3 + O \longrightarrow (NH_4)_2S_4O_6 + 2\,NH_4OH$$

increases to a maximum (No. 4) and is then progressively decomposed by hydrogen sulphide to complete elimination. Thiosulphate increases with the alkalinity in the filtrate to a maximum (No. 5) and is then progressively decomposed to a constant value. The thiosulphate in the precipitate increases to a constant maximum value as expected, no loss being observed *pari passu* with the reduction of concentration of thiosulphate in the filtrate.

This is peculiar to the reaction under consideration and is due to the fact that easily hydrolysable ammonium thiosulphate is decomposed by hydrogen sulphide. In an actual experiment at ordinary temperature, 90% of a 0·2% solution of ammonium thiosulphate was decomposed by passing hydrogen sulphide through it for 5 hours (15-18°).

The transitory presence of tetrathionate as a bye-product was shown, as described in the case of potassium dichromate (*loc. cit.*), by oxidising the filtrate and precipitate with bromine water. By the same method, the absence of tetrathionate from the final product was also established.

It has been proved that potassium trithionate (method of Mackenzie and Marshal, *J. Chem. Soc.*, 1908, **93**, 1732) is not decomposed by hydrogen sulphide and should, therefore, appear in the end-products of that reaction if formed at any stage. There is no thionate present in the final products of the reduction of potassium dichromate by hydrogen sulphide and therefore it is inferred that trithionate is not an intermediate or bye-product in the action of hydrogen sulphide on ammonium dichromate though, like the thiosulphate, ammonium trithionate would be decomposed by hydrogen sulphide.

The action of hydrogen sulphide on ammonium chromate gives similar products, including the intermediate formation of a little tetrathionate which is eliminated in the completed reaction.

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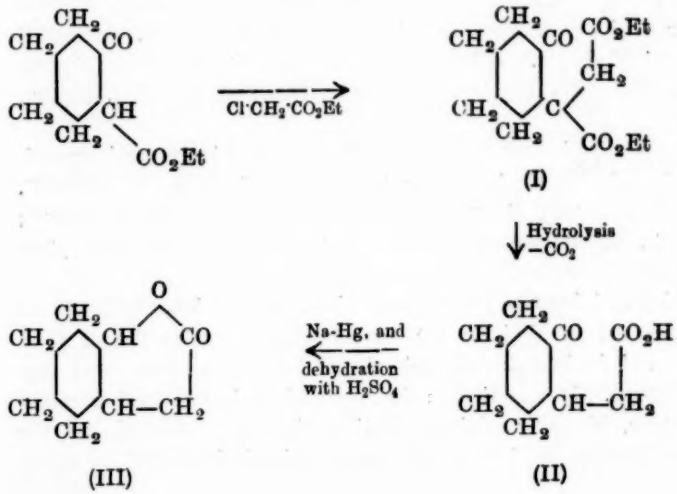
Synthesis of Hexahydro-α-Coumaranone.

By Ranajit Ghosh.

Hexahydro-α-coumaranone, previously obtained by Wallach (*Annalen*, 1907, **353**, 292), Coffey (*Rec. trav. chim.*, 1923, **42**, 387) and also by Braun and Munch (*Annalen*, 1928, **465**, 52), has now been prepared in quantity by a different method, with a view to study Friedel-Crafts' reaction on bicyclic-γ-lactones with aromatic hydrocarbons, phenols, phenol-ethers, etc. (*cf.* Eijkmann, *Chem. Zentr.*, 1904, **I**, 1416; 1905, **I**, 1388; 1907, **II**, 2045) and to convert the resulting products to phenanthrene derivatives.

Ethyl *cyclo*hexanone-2-carboxylate obtained by the method of Kotz (*Annalen*, 1906, **350**, 210) was converted to diethyl *cyclo*hexanone-2-acetate-2-carboxylate (I) by its interaction with ethyl chloroacetate in presence of sodium. *cyclo*Hexanone-2-acetic acid (II), obtained by hydrolysis of the ester, was reduced by means of sodium amalgam and then heated with dilute sulphuric acid yielding the lactone hexahydro-α-coumaranone (III) in good yield.



In order to compare the properties of the above lactone with those of the lactone obtained by Wallach's method (*loc. cit.*) and also by the method of Braun and Munch (*loc. cit.*), $\Delta^{1:2}$-*cyclo*hexene-acetic acid was converted into the lactone in the presence of sulphuric acid according to the method of Linstead and Meade (*J. Chem. Soc.*, 1934, 942) and the lactone is identical with the hexahydro-α-coumaranone described in this paper.

Experimental.

Diethyl cyclo*hexanone*-2-*carboxy*-2-*acetate*.—Finely divided metallic sodium (11·5 g.) in dry benzene (300 c.c.) was slowly treated with ethyl *cyclo*hexanone-2-carboxylate (87 g.) and kept overnight. Ethyl chloroacetate (63 g.) was then added and the mixture refluxed on the water-bath for 5 hours. It was then cooled, washed with water, dried over $CaCl_2$ and the benzene removed and the residual oil was distilled at 161-162°/5 mm., yield 60 g. [Found: C, 60·56; H, 7·9; M. W. (cryoscopic in benzene), 256·3. $C_{13}H_{20}O_5$ requires C, 60·93; H, 7·81 per cent. M. W., 256). The above reaction of *cyclo*hexanone-2-carboxylic ester with chloroacetic ester and sodium ethoxide in alcoholic solution results in poor yield.

cyclo*Hexanone*-2-*acetic acid* was prepared by heating the foregoing ester (50 g.) with concentrated hydrochloric acid (*d* 1·19, 100 c. c.) and water (50 c. c.) for 7 hours. The clear aqueous solution was decanted off and water removed under reduced pressure and the thick reddish brown liquid was distilled at 168-173°/7 mm. (redistilled at 169°-170°/7 mm.), yield 20 g. (Found: C, 61·45; H, 7·75; Equiv., 155·2. $C_8H_{12}O_3$ requires C, 61·55; H, 7·69 per cent. Equiv., 156).

The *semicarbazone* was prepared in aqueous solution and crystallised from ethyl alcohol as colourless needles, m. p. 199-200°. (Found: C, 50·57; H, 7·1; N, 19·58. $C_9H_{15}O_3N_3$ requires C, 50·7; H, 7·04; N, 19·7 per cent). The semicarbazone is acidic and gives effervescence with sodium bicarbonate solution.

Ethyl cyclo*hexanone*-2-*acetate*.—The foregoing keto acid (20 g.) was dissolved in alcoholic solution of sodium ethoxide (3 g. of Na in 200 c. c. of absolute alcohol) and refluxed for 9 hours with ethyl bromide (35 g.). It was then cooled, treated with water and extracted with ether, dried over calcium chloride, the ether removed and the residue distilled at 128-135°/10 mm. (redistilled at 130°/10 mm.),

yield 15 g. [Found: C, 65·18; H, 8·72; M. W. (cryoscopic in benzene), 187. $C_{10}H_{16}O_3$ requires C, 65·21; H, 8·69 per cent. M. W., 184]. The *semicarbazone* crystallised from ethyl alcohol as colourless needles, m. p. 196°. (Found: N, 17·48. $C_{11}H_{19}O_3N_3$ requires N, 17·43 per cent).

Hexahydro-α-coumaranone.—(*a*) *cyclo*Hexanone-2-acetic acid (20 g.) was reduced with sodium amalgam (30%, 400 g.) and a stream of carbon dioxide was bubbled through it. After the sodium amalgam was exhausted, the solution was acidified with dilute sulphuric acid and boiled for some time. The liquid was then cooled and extracted with ether. The ethereal extract was washed with sodium bicarbonate solution, dried over anhydrous sodium sulphate, the ether removed and the residue distilled at 135°-142°/15 mm. (redistilled at 137°/15 mm. or at 130°/10 mm.; *cf.* Coffey, 138-139°/15 mm; Braun and Munch, 129-130°/13 mm.); yield 10 g. [Found: C, 68·51; H, 8·60; M. W. (cryoscopic in benzene) 144. $C_8H_{12}O_2$ requires C, 68·57; H, 8·57 per cent. M. W., 140). The oil is very sparingly soluble in water, does not give effervescence with sodium bicarbonate solution. It dissolves in hot caustic soda solution. It has also a characteristic sweet odour.

(*b*) $\triangle^{1:2}$-*cyclo*Hexene-acetic acid (prepared by Wallach's method, *loc. cit.*) was treated with sulphuric acid and kept at 90° for 30 minutes. It was then cooled and poured into crushed ice, the oil extracted with ether, washed with sodium bicarbonate solution, dried over anhydrous sodium sulphate and after removal of ether, distilled at 135-138°/15 mm. as a colourless oil. [Found: C, 68·48; H, 8·62; M. W. (cryoscopic in benzene), 146. $C_8H_{12}O_2$ requires C, 68·57; H, 8·57 per cent. M. W., 140). Its properties are the same as those described under the lactone obtained by the the method (*a*).

In conclusion I wish to express my sincere thanks to Sir P. C. Rây for the kind interest he took during the investigation and also for placing the resources of his laboratory at my disposal.

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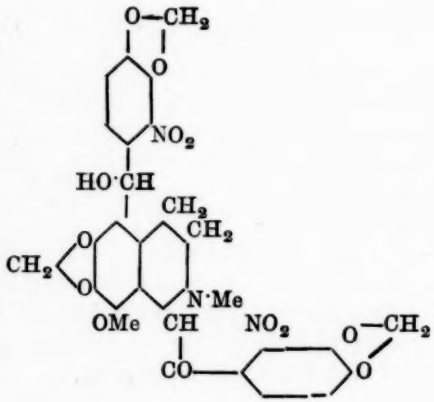
Studies in the Cotarnine Series. Part V. Condensation of Cotarnine with Aromatic Nitro-aldehydes.

By B. B. Dey and (Miss) P. Lakshmi Kantam.

Robinson and Robinson (*J. Chem. Soc.*, 1914, **105**, 1458) condensed cotarnine with 6-nitropiperonal and stated that the product was undoubtedly 6-nitropiperonylhydrocotarnine and thus belonged to a new class of *iso*quinoline derivaties. In a later paper (*J. Chem. Soc.*, 1924, **125**, 840), however, they published a correction regarding the composition of this compound ; they observed that the results of analysis of the product agreed with the assumption that the reaction had occurred between 1 molecule of the base and 2 molecules of the nitro-aldehyde and assigned the following structure to the condensation product on the basis of the well known reactivity of the 5- or *ana*-position in cotarnine :—



This reaction has now been found to be a general one for aromatic nitro-aldehydes, 2 molecules of the nitro-aldehyde condensing with 1 molecule of the base with the elimination of 1 molecule of water. Further, the observation has been made that if position5 in the cotarnine molecule be blocked by a substituent, *e.g.*, the bromine atom, reaction occurs with only 1 molecule of the nitro-aldehyde, thus affording confirmation of the assumption made by Robinson

regarding the point of attachment of the second molecule of the nitro-aldehyde. Attention may be drawn in this connection to the recent work of Ahluwalia, Kaul and Rây (*J. Indian Chem. Soc.*, 1933, **10**, 197) who describe a product (m. p. 154°) which is obviously identical with the compound prepared by us, by the condensation of cotarnine with *o*-nitro-benzaldehyde. Their assumption that the compound is *o*-nitro-benzaldehydo-1-hydrocotarnine seems, however, to be incorrect as the complete analysis of the base and its hydrochloride clearly point to its being derived from the condensation of 2 molecules of the aldehyde with 1 molecule of the base. The formula proposed by the above-mentioned workers appears to have been based on an estimation only of nitrogen in the compound, but as would be seen from a comparison of the percentage values of nitrogen for the two compounds, this determination is not sufficient to enable one to distinguish between the two formulæ.

Experimental.

5-(o-Nitro)-benzaldehydo-1-(o-nitro)-benzoylhydrocotarnine.—Cotarnine (1 g.) and *o*-nitrobenzaldehyde (1·28 g.) in the proportion of 1 to 2 molecules were dissolved in absolute alcohol (12 c. c.) by warming to 50° on the water-bath and the clear solution exposed in a quartz flask to direct sunlight for 3-4 hours. The crystals of a cream colour which separated out were filtered, washed with a little alcohol and dried in the desiccator. The substance was quite pure and melted sharply at 153°, yield 0·8 g. The same product was also obtained in a diminished yield by keeping the mixture in the dark for 24 hours. It is very sparingly soluble in alcohol and in most of the common organic solvents. (Found: C, 60·16; H, 4·65. $C_{26}H_{23}O_9N_3$ requires C, 59·88; H, 4·41 per cent).

The sparingly soluble *hydrochloride* of the base was prepared by dissolving it in glacial acetic acid and adding a few drops of 4 *N*-hydrochloric acid; it separated almost immediately in the form of fine colourless crystals, m. p, 172° (decomp.). (Found: Cl, 7·06. $C_{26}H_{23}O_9N_3$, HCl requires Cl, 6·4 per cent).

The *hydrobromide* of the base, prepared similarly, separated in the form of colourless plates, m. p. 177° (decomp.). [Found: Br, 12·96; H_2O (at 110°/5 mm.), 2·35. $C_{26}H_{23}O_9N_3HBr$, H_2O requires Br, 12·8; H_2O 2·9 per cent]. The *nitrate* separated in the form of prisms, m. p. 181° (decomp.) on the addition of dilute nitric acid to

the glacial acetic acid solution of the base. The *sulphate*, prepared in the same manner, crystallised in clusters of prisms, m. p. 191-92° (decomp.). The *picrate* separated in short thin yellow needles, m. p. 175-76°.

5-(o-*Amino*)-*benzaldehydo*-1-(o-*amino*)-*benzoylhydrocotarnine*.—The well powdered nitro-compound (1 g.) was gradually added to a mixture of stannous chloride (3 g.), hydrochloric acid (5 c. c.) and a small piece of granulated tin and the whole shaken for a few hours. Water (50 c. c.) was added, the clear liquid was basified with excess of 25% sodium hydroxide, and the separated solid washed with water, dried on a porous plate and then in the desiccator and the dry solid, extracted with warm benzene (60°). The amino compound separated from the benzene solution as a pale yellow crystalline solid, m. p. 122°. On diazotising its solution in cold hydrochloric acid and coupling with β-naphthol, a deep red dyestuff was thrown down. (Found:: C, 68 2 ; H, 5·88. $C_{26}H_{27}O_5N_3$ requires C, 67·68; H, 5·85 per cent). The *diacetyl* derivative of the amine separated from alcohol as a colourless crystalline powder, m.p. 126°.

5-(m-*Nitro*-)-*benzaldehydo*-1-(m-*nitro*-)-*benzoylhydrocotarnine* separated in a crystalline form on warming an alcoholic solution of cotarnine (1 mol.) and *m*-nitrobenzaldehyde (2 mols.) to 60° for 1 hour and then leaving at room temperature for 2 days. The crystals, after washing with cold alcohol, were pure and melted at 146°. It was sparingly soluble in the common organic solvents. (Found: C, 60·17 ; H, 4·76. $C_{26}H_{23}O_9N_3$ requires C, 59·88 ; H, 4·41 per cent). It formed a sparingly soluble hydrochloride crystallising in plates, m.p. 188° (decomp). (Found: Cl (HCl), 6·25. $C_{26}H_{23}O_9N_3$, HCl requires Cl, 6·4 per cent).

5-(m-*Amino*-)-*benzaldehydo*-1-(m-*amino*-)-*benzoylhydrocotarnine*.—The nitro-compound was reduced and the product isolated in the same manner as the corresponding *ortho*-compound. The amine, m.p. 113°, dissolved easily in benzene and gave an azo-dye in the usual way.

5-(6-*Nitro*-3 : 4-*dimethoxy*)-*benzaldehydo* 1-(6-*nitro*-3 : 4-*dimethoxy*)-*benzoylhydrocotarnine*, prepared in the same way from cotarnine and nitrovanillin methyl ether, formed yellow crystals, m.p. 168°. (Found: C, 55·38 ; H, 4·94. $C_{30}H_{31}O_{13}N_3$ requires C, 56·1; H, 4·83 per cent). The *hydrochloride* of the base, m.p. 193° (decomp.) was sparingly soluble in water. [Found: Cl (HCl), 4·69. $C_{30}H_{31}O_{13}N_3$. HCl requires Cl, 5·23 per cent].

1-(*o-Nitro-*)-*benzoyl-5-bromohydrocotarnine*.—A mixture of 5-bromocotarnine (1 g., 1 mol.) and *o*-nitrobenzaldehyde (0·9 g., 2 mols.) dissolved in absolute alcohol (10 c.c.) was exposed to direct sunlight for 4 hours. The solution was then poured into water (50 c.c.), when an oil separated out which hardened to a gritty solid after 24 hours. It was purified by dissolving in cold acid and reprecipitating with caustic soda, and tnen crystallising from alcohol by dilution with water. It formed indefinite crystals, m.p. 120°, sintering a few degrees before this temperature. Repeated purification from alcohol, however, did not improve the m.p. (Found: N, 6·93. $C_{19}H_{17}O_6N_2Br$ requires N, 6·24 per cent).

The sparingly soluble *hydrobromide* of the base separated as crystals on adding a solution of hydrobromic acid to the base in glacial acetic acid, m.p. 162° (decomp.). [Found: Br (HBr), 15·33. $C_{19}H_{17}O_6N_2$ Br, HBr requires Br (HBr), 15·09 per cent].

5-(6-*Nitro*)-*piperonoyl*-1-(6-*nitro*) *piperonoyl hydrocotarnine* (Robinson, *J. Chem. Soc.*, 1914, **105**, 1468).—Cotarnine (1 g.) and 6-nitropiperonal (1·64 g.) were dissolved in alcohol (10 c.c.), slightly warmed on the water-bath and exposed to sunlight. A greenish yellow crystalline solid began to separate after an hour. The solid was filtered, washed with alcohol and crystallised from a mixture of pyridine and alcohol as a yellow crystalline powder sparingly soluble in alcohol, m.p. 168°. The *hydrobromide* of the base, prepared as before, melted at 180° (decomp.). (Found: Br, 12·25. $C_{28}H_{23}O_{13}N_3$, HBr requires Br, 11·58 per cent).

1-(6-*Nitro-*) -*piperonoyl-5-bromohydrocotarnine*.— 5- Bromocotarnine (1 g.) and 6-nitropiperonal (0·62 g.) were mixed with rectified spirit (15 c.c.), slightly warmed till a clear solution was obtained and left for 24 hours. The yellow crystalline solid was collected and washed with cold alcohol, in which it was almost insoluble, m.p. 125°. (Found: N, 5·95. $C_{20}H_{17}O_8$ N Br requires N, 5·68 per cent). The hydrobromide of the base melted at 172°. [Found: Br, 13·3. $C_{20}H_{17}O_8N_2Br$, HBr requires Br (HBr) 13·93 per cent].

On attempting the condensation of *o*-nitro-aldehydes with hydrocotarnine and narcotine in alcoholic medium in exactly the same way, only unehanged materials were recovered.

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On the Triple Nitrites of the Rare Earths and a New Micro-test for Cæsium.

By Harish Chandra Goswami and Pulin Bihari Sarkar.

The ingenious method of isolation of spectroscopically pure europium, gadolinium and terbium effected by Prof. Urbain by the use of Bi "comme élément séparateur" is based on the isodimorphism of hydrated bismuth nitrates with the rare-earth nitrates and the isomorphism of the double nitrates of bismuth of the type $2M_1(NO_3)_3$, $3M_2(NO_3)_2,24H_2O$ where M_1 may be Bi or Σ La up to Ga, and M_2 may be Mg, Zn, Ni, Co or Mn.

Ball and Abram (*J. Chem. Soc.*, 1913, **103**, 2110) prepared a number of complex bismuthinitrites of the types $X_3Bi(NO_2)_6$ and $X_2Y\,Bi(NO_2)_6$ where X stands for NH_4, K, Rb, Cs and Tl, and Y for Li, Na or Ag.

Our knowledge of the nitrites of the rare-earths is extremely meagre. This led the authors to investigate whether cerium and other rare-earth elements form triple nitrites analogous to those of bismuth. The following triple nitrites of the formula $Cs_2NaR(NO_2)_6$ (where R=Ce, La, Pr, Na, Sm or Gd) have been prepared and described in the paper. The elements of the yttrium group beyond gadolinium do not form such nitrites. These are sparingly soluble octahedral crystals stable at the ordinary temperature. Their aqueous solutions are slowly hydrolysed. The formation of these octahedral triple salts may be used for the micro-detection of cæsium. The test appears to be specific for Cs since potassium and rubidium do not respond.

Experimental.

Cæsium-sodium-cerium nitrite—Cerous nitrate solution (50%, 10 c.c.) was mixed with sodium nitrite solution (50%, 10 c. c.) and the mixture was filtered. To the filtrate, 10 c.c. of a cæsium nitrate solution (10%) were then stirred in and the solution kept in a stoppered bottle. After 4 hours, the yellow crystals were drained, washed, first with a sodium nitrite solution (10%), then with a mixture of acetone

and water and finally with acetone. They were then dried in a desiccator. The salt is stable in air at the ordinary temperature but decomposes gradually when heated to 100°. [Found: N, 11·98; Cs, 37·70; Ce, 20·06; Na, 3·29. Cs_2 Na $Ce(NO_2)_6$ requires N, 11·90; Cs, 37·70; Ce, 19·88; Na, 3·26 per cent].

Cæsium-sodium-lanthanum nitrite.—The method of preparation is similar to that of the preceding salt. [Found: Cs, 37·78; La, 20·0; Na, 3·2. $Cs_2NaLa(NO_2)_6$ requires Cs, 37·77; La, 19·74; Na, 3·27 per cent].

Cæsium-sodium-praseodymium nitrite.—The method of preparation is similar to above. The triple salt was obtained in the form of pale green octahedral crystals. [Found: Cs, 37·89; Na, 3·15; Pr, 20 0. Cs_2Na Pr $(NO_2)_6$ requires Cs, 37·66; Na, 3·26; Pr, 19·96 per cent].

Cæsium-sodium-neodymium nitrite was separated exactly as the previous one. [Found: Cs, 37·65; Na, 3·05; Nd, 20·21. $Cs_2NaNd(NO_2)_6$ requires Cs, 37·49; Na, 3·24; Nd, 20·35 per cent].

Cæsium-sodium-samarium nitrite was prepared exactly as praseodymium and neodymium salts. [Found: Cs, 37·4; Na, 3·16; Sm, 21·29. Cs_2NaSm $(NO_2)_6$ requires Cs, 37·16; Na, 3·21; Sm, 21·03 per cent].

Cæsium-sodium-gadolinium nitrite was prepared as the preceding ones. [Found: Cs, 36·70; Gd, 21·69; Na, 3 18. $Cs_2NaGd(NO_2)_6$ requires Cs, 36·80; Gd, 21·78; Na, 3·16 per cent].

Method of analysis.—The salts were decomposed with concentrated HCl and the rare-earths were precipitated as hydroxides by double precipitation with ammonia. The precipitated hydroxides were filtered, dissolved in dilute HNO_3 and precipitated as oxalates. They were then ignited and weighed as oxides. From the filtrate ammonium salts were removed and the total alkali metals were weighed in the form of sulphates. Sodium was estimated as sodium-magnisium-uranyl acetate and cæsium was determined by difference. Nitrogen was estimated by conversion to ammonia by distillation with zinc and alkali and subsequent absorption in standard acids.

Micro-detection of cæsium.—All the triple nitrites described in this paper furnished a ready method for the micro-detection of cæsium. The praseodymium salt appears to be best suited for the purpose since it is the most stable of the series.

Reagent.—3 G. of praseodymium nitrate and 10 g. of sodium nitrite were dissolved in 100 c.c. of water. The solution was then filtered and preserved in a well-stoppered bottle.

Procedure.—A drop of the reagent was taken on a microscope slide and was touched with a small platinum loop dipped in a solution of cæsium nitrate. After 3 or 4 minutes, beautiful octahedral crystals appear when viewed through a microscope (magnification 400 times). The limit of identification has been measured to be 4×10^{-8}g. (0·04γ). The test is specific for cæsium, rubidium and potassium do not interfere. It appears to be more sensitive than the triple cæsium-silver-gold chloride test advocated by Emich. It is advisable to use the alkali (cæsium) salt in the form of a nitrate.

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Condensation of Cotarnine and *o*-Nitrobenzaldehyde.

BY K. N. KAUL AND G. S. AHLUWALIA.

Ahluwalia, Kaul and Rây (*J. Indian Chem. Soc.*, 1933, **10**, 197) have condensed cotarnine with *o*-nitrobenzaldehyde and formulated the product as *o*-nitrobenzoylhydrocotarnine following Robinson and Robinson (*J. Chem. Soc.*, 1914, **105**, 1458). A later note of Robinson and Robinson (*J. Chem. Soc.*, 1924, **125**, 840), in which this formulation has been modified, escaped our attention. The analytical values for nitrogen come within experimental error whether $C_{26}H_{23}O_9N_3$ or $C_{19}H_{18}O_6N_2$ is accepted. A carbon hydrogen determination was considered unnecessary because it was not realised that there could be anything wrong with Robinson and Robinson's formulation.

Our attention has been drawn to this later note of Robinson and Robinson. Therefore we desire to correct our fomulation of the condensation product and bring it in line with the later formula of these authors.

In fact we stated that " following Robinson and Robinson (*J. Chem. Soc.*, 1914, **105**, 1458) the compound was formulated as I " (*loc. cit.*).

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On the Supposed Occurrence of Acids with Uneven Number of Carbon Atoms in Vegetable Oils and Fats. Part II. The Acid Fraction of Mean Molecular Weight 354, from the Seeds of *Butea Frondosa* (Roxb).*

By U. S. Krishna Rao and B. L. Manjunath.

During the examination of the fatty oil from the seeds of *Butea frondosa*, Katti and Manjunath (*J. Indian Chem. Soc.*, 1929, **6**, 839) identified among the solid acids, palmitic and lignoceric acids only and isolated two fractions A and B, the first of which melted at 74·5-75·5° and had the mean mol. wt. 353 and the second melted at 77 5-79° and had the mean mol. wt. 383. The present investigation is concerned with the nature of the fraction A.

Katti and Manjunath (*loc. cit.*) found strong evidence in favour of the individuality of this fraction. They pointed out that *n*-tricosoic acid synthesised by Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 921) melted at 80-81° and that the lower melting point of the fraction A may be due to small admixtures of a lower acid and lignoceric acid.

Manjunath and Siddappa (*J. Indian Chem. Soc.*, 1935, **12**, 495) have been unable to obtain any evidence regarding the existence of Daturic acid ($C_{17}H_{34}O_2$) in the oil of the seeds of *Datura stramonium*. Nöller, Milner and Garden (*J. Amer. Chem. Soc.*, 1933, **55**, 1227) have separated the so-called 'Umbellulic acid' (Stillman and Neill, *J. Amer. Chem. Soc.*, 1902, **28**, 327) into capric and lauric acids. Since recent researches have thrown considerable doubt on the occurrence of acids with uneven number of carbon atoms in vegetable oils and fats, it was thought of interest to establish if the acid fraction A was really tricosoic acid or an eutectic mixture of acids.

* Taken from the thesis submitted by U. S. K. Rao for the degree of Master of Science in the University of Mysore.

Experimental.

25 G. of the purified acid A (m. p., 74·5-75·5°; M. W., 353) were esterified with methyl alcohol and the ester (m. p. 54-55°) was fractionated in high vacuum. The results confirmed the observations of Katti and Manjunath (*loc. cit.*). The acid liberated from the residues (2 g.) in the distillation flask on repeated crystallisation melted at 78-79°. Its molecular weight was 366. It did not depress the m. p. of pure lignoceric acid and its *p*-phenylphenacyl ester (m. p. 102-103°) and *p*-bromophenacyl ester (m.p. 93-94°) (Found: C, 68·1; H, 9·6. $C_{32}H_{53}O_3Br$ requires C, 68·0; H, 9·4 per cent) were found to be the same as those prepared from pure lignoceric acid.

Experiments were then made to prepare *p*-phenylphenacyl and *p*-bromophenacyl esters from fraction A. The former melted at 98·5-99° (Found: C, 80·9; H. 10·2. $C_{37}H_{56}O_3$ requires C, 81·0; H, 10·2 per cent) and the latter at 90·5° (Found: C, 67·5; H, 9·2. $C_{31}H_{51}O_3$ requires C, 67·5; H, 9·2 per cent). Repeated attempts at fractional crystallisation from various solvents did not effect any separation and the results appeared to point towards the individuality of A.

We may note here that the *p*-phenylphenacyl and *p*-bromophenacyl derivatives are unsuitable for the characterisation of the higher fatty acids as may be seen from the mixed melting points given below:

Table I.

No.	*p*-Phenylphenacyl ester of	M. p.	Mixed m. p. with
1	Palmitic acid	93-94°	(2) 90-90·5°; (4) 90-93°
2	Stearic acid	95·5-96·5°	
3	Behenic acid*	101-102°	(4) 98-99·5°; (5) 100-101°
4	Lignoceric acid	101-102°	(5) 100-100·5°
5	Fraction A	98·5-99°	

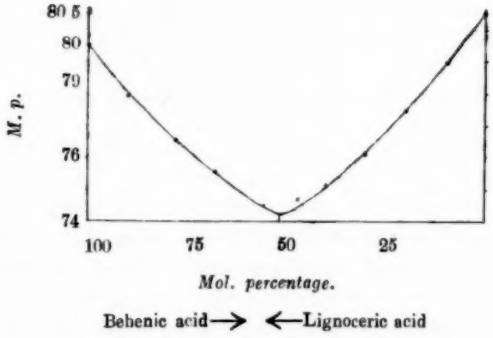
* (Found: C, 80·9; H, 10·3. $C_{36}H_{54}O_3$ requires C, 80·9; H, 10·1 per cent).

TABLE II.

No.	*p*-Bromophenacyl ester of	M. p.	Mixed m.p. with
1	Palmitic acid*	83–84°	(2) 76–78°; (4) 84–86°
2	Stearic acid†	87·5–88·5°	
3	Behenic acid‡	93–94°	(4) 90·5–91°; (5) 91–92°
4	Lignoceric acid	93–94°	(5) 91–91·5°
5	Fraction A	90·5°	

Since identification in this manner proved inconclusive, the melting point curves of mixtures of palmitic and lignoceric acids, stearic and lignoceric acids were determined in order to find out if any evidence regarding the formation of an eutectic mixture could be obtained. Behenic acid for this purpose was prepared by the catalytic reduction of erucic acid** in the presence of nickel.

FIG. 1.



* (Found : C, 63·6; H, 8·1. $C_{24}H_{37}O_3Br$ requires C, 63·5; H, 8·2 per cent).

† (Found : C, 64·9; H, 8·7. $C_{26}H_{41}O_3Br$ requires C, 64·9; H, 8·6 per cent) Judefind and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1054) have prepared these two esters and give the melting point of the former as 81·5° and of the latter as 78·5°.

‡ (Found : C, 67·1; H, 9·2. $C_{30}H_{49}O_3Br$ requires C, 67·0; H, 9·1 per cent).

** p-*Phenyl phenacyl ester*, m. p., 72·5-73·5°. (Found : C, 81·3 ; H, 9·6. $C_{36}H_{52}O_3$ requires C, 81·2; H, 9·8 per cent).

p-*Bromophenacyl ester*, m. p. 60-60·5°. (Found; C, 67·4 ; H, 8·8. $C_{39}H_{47}O_3Br_2$ requires C, 67·3; H, 8·8 per cent).

FIG. 2.

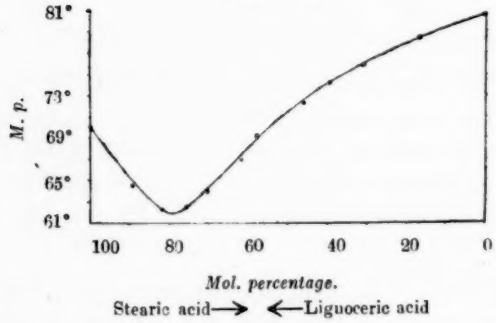
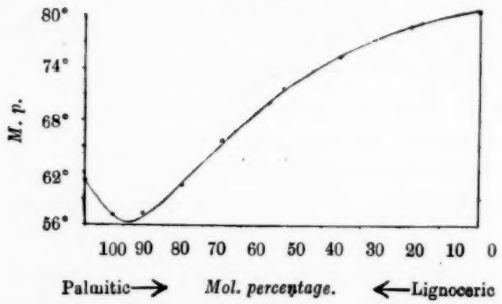


FIG. 3.



From the three curves (Fig. 1-3) it became clear that behenic and lignoceric acids in equimolecular proportions form an eutectic mixture melting at 74-75°. Consequently an equimolecular mixture of behenic acid and lignoceric acid (m. p. 89·5 ; M. W., 370) was prepared and experiments were carried out to separate the synthetic mixture into its constituents.

Repeated crystallisations from various solvents, fractional precipitation of the lithium salts, or the high vacuum distillation of the methyl esters did not bring about any separation. In the last case as with A, a small amount of pure lignoceric acid was obtained from the residue in the flask.

(1) Repeated crystallisations from methyl and ethyl alcohols, acetone and ethyl acetate did not bring about a change either in the melting point or in the mean molecular weight.

(2) Fractional precipitation of the lithium salts also did not effect separation.

TABLE III.

Fraction No.	M. p. of acids liberated and crystallised.	Molecular weight.
1	75–76°	352·0
2	74–75·5°	354·2
3	74–75°	357·8
4	73·5–75°	357·0

(3) This mixture (22 g.) was converted into the methyl ester (28 g.) and the methyl ester (m. p. 55-56°) was fractionally distilled at a pressure of less than 1 mm.

Fraction No.	Range of temperature.	Wt. of fraction.	M. W. from sap. value	M. p. of acid liberated and crystallised.
1	below 198°	2·8 g.	352·2	74-75°
2	at 198°	6·1	356·7	74·5-75·5°
3	198–200°	7·2	354·9	74·5-75·5°
4	200–202°	4·0	358·3	75-76°
Residue		2·9		

A small quantity of pure lignoceric acid (2 g.) was obtained from the residue after saponification and repeated crystallisations.

Thus it was found impossible to effect satisfactory separation of the eutectic mixture of behenic and lignoceric acids.

CONCLUSION.

The fraction A is in all probability an eutectic mixture of behenic and naturally occuring lignoceric acids in equimolecular proportions and is not an individual substance. Similarly it is also highly probable that fraction B is an eutectic equimolecular mixture of lignoceric and cerotic acids. This latter acid has been found to occur sometimes in small quantities in vegetable products and forms probably another eutectic mixture of the type met with in fraction A.

As a result of this investigation the occurrence of behenic and cerotic acids in the oil of *Butea frondosa* is indicated.

We are indebted to Mr. P. Ramaswami Iyer for the lignoceric acid used in this investigation.

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Metallic Uranium in Organic Synthesis. Part II.

By Jagraj Behari Lal.

Very recently uranium metal has been introduced in organic synthesis and has been successfully used in Friedel-Crafts', Reformatsky's and Zincke's reactions. It did not give very encouraging results in Ullmann's reaction (Lal and Dutt, *J. Indian Chem. Soc.*, 1935, **12**, 389) but highly satisfactory results were obtained in Zincke's reaction where the action of benzyl chloride on hydrocarbons and phenolic ethers was tried. In the present investigation the action of benzyl chloride on toluene, phenol, hydroquinone dimethyl ether, and on higher hydrocarbons such as naphthalene, acenaphthene and diphenyl in presence of uranium metal has been successfully tried and the various products isolated. The study of these reactions is complicated by the fact that in addition to the isomeric monobenzyl derivatives, isomeric dibenzyl derivatives are simultaneously formed during the reaction, isolation and characterisation of which becomes consequently a difficult task.

The action of benzyl chloride on naphthalene was first studied by Fröte in presence of zinc dust (*Compt rend.*, 1873, **76**, 639) and then Mignal (*Bull. Soc. chim.*, 1877, *ii*, **25**, 27), Vincent and Roux (*ibid.*, 1883, **40**, 163) and Roux (*Ann. chim. phys.*, 1887, *vi*, **12**, 289) studied the reaction using zinc dust, fused zinc chloride and anhydrous aluminium chloride respectively as the catalyst. The later authors isolated pure α- and β- benzylnaphthalenes. Boguski (*Ber.*, 1906, **39**, 2866) using metallic aluminium isolated in addition to the two monobenzylnaphthalenes, a dibenzylnaphthalene (m. p. 146·5°).

Dziewonski and Moszew (*Bull. Acad. Polonaise*, 1928, **A**, 283) and Wodelski (*Rocz. Chem.*, 1932, **12**, 266) have isolated several dibenzylnaphthalenes. The mono- and dibenzylnaphthalenes have further been studied in great detail in recent years (*Bull. Acad. Polonaise*, 1927, **A**, 273-286 ; 1928, **A**, 283 ; 1930, **A**, 66 ; *Rocz. Chem.*, 1929, **9**, 361).

By the action of benzyl chloride on acenaphthene and diphenyl in presence of uranium, 5-benzylacenaphthene and β-(3 or 4) benzylacenaphthene and two benzyldiphenyls (m. p. 44-45° and 51-55°) have been isolated respectively.

Attempts were also made to prepare hexanitrodiphenyl from picryl chloride, 4:4'-dinitrodiphenyl from *p*-nitrochlorobenzene but without success. It has also been found that uranium metal cannot be used as neutral reducing agent either in aqueous or aqueous-alcoholic solutions.

Unsuccessful Attempts.

Type of reaction.	Reactants.	Expected products.
1. Ullmann's	Picryl chloride	Hexanitrodiphenyl
2. ,,	*p*-Nitrochlorobenzene	4:4'-Dinitrodiphenyl
3. Neutral reduction	Benzophenone	Benzhydrol
4. ,,	Nitrobenzene	Aniline
5. ,,	*p*-Nitrotoluene	*p*-Toluidine
6. ,,	Picric acid	Picramic acid
7. Zincke's reaction	Benzyl chloride and benzyl cyanide	Benzyl benzyl-cyanide.

Experimental.

Benzylhydroquinone dimethyl ether.—A mixture of hydroquinone dimethyl ether (16 g.), benzyl chloride (10 g.) and uranium dust (3 g.) was gradually heated in an oil-bath up to 70° when hydrogen chloride was freely evolved. After the first vigorous reaction had subsided the mixture was heated at 110°-120° for 4 hours. The product was extracted with benzene, filtered, washed with water and dried over calcium chloride, and after removal of benzene it was fractionated at ordinary pressure and the fraction at 340°-360° (redistilled at 353°-355°) was identified as benzylquinol dimethyl ether, yield 12·6 g. (66·3%). A deep red viscous residue was left in the distilling flask and on standing for about a month deposited a small amount of a crystalline mass (0·8 g.). It crystallised from boiling alcohol as rhombic tablets, m. p. 104-5° and is under investigation.

o- & p-*Benzylphenols.*—Benzyl chloride (16 g.), anhydrous phenol (21 g.) and uranium dust (3·5 g.) were heated first at 70° for ½ an hour when a very vigorous reaction took place and then at 120°-130° for 4 hours. The product was filtered hot and then fractionated at ordinary pressure and the fractions boiling at 305°-330° and 360°-370° collected. By repeated fractionation the fraction (b. p. 305-330°) was separated into two fractions (A) distilling at 310-12° and (B) at 320-22°. The fraction (A) crystallised on standing, and the crystals after being pressed between filter papers melted at 20°

and were identified as those of benzylphenol, yield 3 g. (*cf.* Claisen, *Z. angew. Chem.*, 1923, **36**, 478.

The fraction (B) was a colourless, non-fluorescent thick heavy liquid with fine floral smell, and insoluble in and heavier than water and it dissolvs in caustic alkalis but not in ammonia. It crystallised from alcohol in shining plates, m. p. 84°, identified as *p*-benzylphenol (the methyl ether, b. p. 304-5°; the mononitro derivative, m. p. 74-75°), yield 18·7 g. (*cf.* Paterno, *Gazzetta*, 1872, **2**, 1; Paterno and Fileti, *ibid.*, 1873, **3**, 121, 251; Rennie, *J. Chem. Soc.*, 1882, **41**, 33). (Found C, 84·39; H, 6·61, $C_{13}H_{12}O$ requires C, 84·78; H, 6·52 per cent.)

The fraction at 360-370° (redistilled at 365-67°) which was free from phenolic compounds was identified as *p*-benzylphenol benzyl ether, yield 2·2 g.

Phenyltolylmethane and dibenzyltoluenes from benzyl chloride and toluene.—A mixture of benzyl chloride (25 g.), toluene (46 g.) and uranium dust (4 g.) was gradually heated in an oil-bath up to 90° when a very vigorous reaction took place. After the first vigorous reaction the mixture was heated at 125-135° for 4 hours and filtered hot. The green filtrate having an intense deep violet fluorescence was washed with water, dried and fractionally distilled at ordinary pressure up to 220° and the residue left in the flask fractionated under reduced pressure of 160 mm:

(1) 95-190°; (2) 190-270°; (3) 270-320° temperature rising quickly; (4) 320-330°; (5) 330-380°/30 mm. The fraction (1) was fractionally distilled at ordinary pressure and the fraction above 270° collected and mixed with fraction (2) and fractionally distilled thrice, finally the fraction at 277-279° was identified as pure *p*-benzyltoluene (yield 20 g., 45·5%). (Found: C, 92·04; H, 7·72. Calc. for $C_{14}H_{14}$. C, 92·30; H, 7·69 per cent). It did not solidify even on keeping in a refrigerator for weeks. In chloroform solution it gave with anhydrous $AlCl_3$ a pink colouration (*cf.* Zincke, *Ber.*, 1874, **7**, 982).

The fraction (4) was a thick liquid with intense violet flourescence and having a fine flowery smell. It was redistilled under reduced pressure and the fraction at 280-285°/30 mm. boiling at 392-396° at ordinary pressure was identified as dibenzyltoluene (11 g.). It was a fluorescent oil which did not solidify even on keeping in a refrigerator for weeks. It dissolved in the usual organic solvents and did not form a picrate. (Found: C, 92·3 ; H, 7·41. Calc. for $C_{12}H_{20}$, C, 92·64; H, 7·35 per cent) (*cf.* Weber and Zincke, *Ber.*, 1874, **7**, 1153).

The portion of the first fraction which distilled at 280-300° at ordinary pressure (1 g.) was fractionated and the various fractions did not solidify even when kept in a freezing mixture while dibenzyl, the possibility of formation of which is not remote, boils at 284° and melts at 52°. So evidently dibenzyl does not appear to be formed.

α- & β- Benzylnaphthalenes.—A mixture of benzyl chloride (30 g.), naphthalene (42 g.) and uranium powder (5 g.) was gradually heated in an oil-bath up to 65° when a very vigorous reaction took place and then maintained at 120-125° for 3 hours. The pink mixture having an intense blue fluorescence was filtered hot from the metal and then fractionated at ordinary pressure, two fractions A (b.p. 310-365°) and B (b.p. 370-76°) being collected. The fraction (A) was steam distilled in order to free it from traces of naphthalene and then extracted with chloroform and after removal of the latter it was fractionally distilled. A small amount of a colourless oil came over at 300-320° and then the rest of the liquid distilled at 340°-355° and both these oils solidified on keeping in a refrigerator. The fraction boiling at 340-355° after crystallisation from boiling alcohol gave α-benzylnaphthalene (16 g.) as rhombic plates, m. p. 57-58°. These were soluble in chloroform, ether, benzene, carbon disulphide and boiling alcohol and on oxidation with concentrated boiling nitric acid gave α-naphthylphenylketone, m. p. 73-73·5° ; picrate, m. p. 99-100° (*cf.* Roux, *loc. cit.*). The fraction at 300-320° after several crystallisations from boiling alcohol gave β-benzylnaphthalene, m. p. 39-40°. It is soluble in benzene and chloroform even in the cold and identified as β-benzylnaphthalene (2 g.).

From the fraction (B) none of the three α, β- and γ- dibenzylnaphthalenes could be isolated.

Phenylacenaphthylmethanes.—A mixture of benzyl chloride (20 g.), acenaphthene (32 g.) and uranium powder (4 g.) was gradually heated in an oil-bath up to 95° when torrents of hydrogen chloride were evolved and after the first vigorous reaction had subsided the temperature of the bath was maintained at 100-110° for 6 hours. The reaction product was extracted with benzene, filtered and after complete removal of benzene fractionally distilled at 15-20 mm., and two fractions collected: (A) b.p. 250-290°, colourless oil, temperature remaining constant at 260-270°; (B) b.p. 300-370°, red oil which did not solidify.

Fraction (A) on redistillation gave a colourless oil (b.p. 260-270°/20 mm.) and on standing it became semi-solid due to the separation of a crystalline mass. After several crystallisations from boiling alcohol the more insoluble portion was obtained as silky white needles, m.p. 106-107° and was identified as 5-benzylacenaphthene (4·2 g.), m.p. 110-11° (*cf.* Dziewonski and others, *Bull. Soc. chim.* 1904, *iii*, **31**, 373; *Bull. Acad. Polanaise*, 1928, **A**, 99). The soluble portion was obtained as needles, m.p. 47-49° (picrate, m.p. 100-101°). It was identified as β- (3 or 4)-benzylacenaphthene (3·4 g.). It melts at 45-46° and forms a dipicrate, m.p. 101-102°. The fraction (3) weighed 14 g. and nothing crystalline could be isolated from it.

α - & β-Benzyldiphenyls.—A mixture of benzyl chloride (14 g.), diphenyl (23 g.) and uranium powder (3 g.) was slowly heated in an oil-bath up to 70° when a very vigorous reaction took place. It was then heated for 4 hours at 120-125°, filtered hot and the filtrate kept in a vacuum desiccator over caustic potash in order to remove the hydrogen chloride present. The product was fractionally distilled at 20 mm. and the fractions collected were: (A) 112-200°, colourless oil, the main fraction coming over at 128-135° and solidifying in the receiver; (B) 200-250°, colourless oil solidifying in the receiver. (C) 340-370°, pale yellow oil which did not solidify even in a freezing mixture (10·8 g.).

Fraction (A) was submitted to redistillation and the fraction below 160° was rejected and the rest redistilled along with (B) when major portion of it distilled at 170-180°. The fraction (*a*) was a colourless oil quickly solidifying on cooling and a second fraction (*b*) at 200-230° was a colourless viscous oil (2·3 g.) which did not solidify immediately. The boiling point of pure diphenyl was found to be 130-132°/20 mm. and the rejection of fraction distilling below 150° ensured the absence of diphenyl in the fraction 170-180°. The fraction (*a*) separated from boiling alcohol in the form of tiny needles, and the first and the least soluble portion on crystallisation from glacial acetic acid was obtained in the form of beautiful long needles, m. p. 44-45° after drying in a vacuum desiccator over caustic potash and was identified as α-benzyldiphenyl. Even after repeated crystallisations from alcohol and acetic acid its melting point remained unaltered. (Found: C, 93·39; H, 6·65. $C_{19}H_{16}$ requires C, 93·44; H, 6·65 per cent). The alcoholic mother liquor gave another crop of crystals after concentration, m. p. 51-56°, β-benzyldiphenyl identical with *iso*benzyldiphenyl of Goldschmidt (*Monatsh.*, 1881, **2**, 432) who by the action of benzyl

chloride on diphenyl in presence of zinc dust isolated *p*-benzyldiphenyl as flat needles from hot glacial acetic and as plates from alcohol, m.p. 85° and *iso*benzyldiphenyl as monosymmetrical needles, m.p. 54°.

The author wishes to convey his heartiest thanks to Dr. S. Dutt, D.Sc., P.R.S. for his keen interest in this investigation.

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A Short Note on the Chromium Biguanide Complexes.

BY PRIYADA RANJAN RÂY AND HARIBOLA SAHA.

Complex compounds of biguanide with bivalent copper, cobalt and nickel have been described long ago (Rathke, *Ber.*, 1878, **11**, 967; 1879, **12**, 777; Rackmann, *Annalen*, 1911, **376**, 168). The constitution of these compounds is, however, still under dispute. As these compounds are very sparingly soluble in water, the study of their constitution by usual physico-chemical methods is rendered thereby extremely difficult.

We have now, however, succeeded in preparing soluble biguanide complexes of tervalent chromium. The free complex base, which forms the mother substance and from which a series of salts is in the course of preparation, has been obtained as beautiful ruby-red crystals of the following composition: $[Cr(C_2N_5H_6)_3]$ H.OH, the biguanide molecule acting as a bidentate group and occupying two co-ordinate positions. The compound is, therefore, expected to give rise to optically active enantiomers. The substance is strongly basic and in aqueous solution behaves as a tri-acidic base, as could be concluded from the freezing-point and conductivity data as well as from the titer-value of the base in aqueous solution.

Fuller details about the preparation, properties and constitution of the compound and its derivatives will be published in due course.

Similar compounds with tervalent cobalt atom have also been prepared and will form the subject matter of a separate paper.

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Synthesis of Coumarins from Phenols and β-Ketonic Esters. Part IV. Coumarins from 4-Chloro- and 2-Nitroresorcins.

By Dukkhaharan Chakravarti and Baidyanath Ghosh.

It has been shown by one of us (Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 120, 407, 619; 1932, **9**, 25, 31, 389) that phenols which react with difficulty to form coumarins (*e.g.*, phenol, *p*-cresol, halogenated phenols) or do not react at all (*e.g.*, *o*-cresol, nitrophenols, guaiacol, hydroquinone) using sulphuric acid as the condensing agent, yield with phosphorus pentoxide chromones.

It seemed of interest to study the behaviour of negatively substituted resorcinols, pyrogallols, phloroglucinols, naphthols, *p*-and *m*-cresols, which have the faculty of the formation of coumarins with great readiness in Pechmann's reaction in view of the generalisation made by Clayton (*J. Chem. Soc.*, 1908, **93**, 2018) that the presence of a halogen atom in the phenolic nucleus greatly hinders Pechmann's reaction and the presence of a negative substituent like NO_2 or COOH totally inhibits the reaction. The present investigation describes the condensation of chlororesorcin and nitroresorcin with alkylacetoacetic esters both in presence of sulphuric acid and phosphorus pentoxide. It is remarkable that even if there be a halogen atom or any other negative substituent in resorcinol, the reaction takes place smoothly forming substituted coumarins.

Chlororesorcin (b.p. 259°; m.p. 88·5-89°), prepared according to the method of Reinhard (*J. pr. Chem.*, 1878, *ii*, **17**, 336) by the action of sulphuryl chloride on a dry ethereal solution of resorcin, has been proved to be 4-chlororesorcin (Clark, *J. Amer. Chem. Soc.*, 1933, **55**, 319). It condenses with acetoacetic ester to form 6-chloro-7-hydroxy-4-methylcoumarin. The introduction of the chlorine atom in the molecule of resorcin does not in any way hinder the reaction and the yields of coumarins from 4-chlororesorcin are in some cases higher than the corresponding yields from resorcin.

As chlororesorcin forms coumarins with good yields in presence of sulphuric acid, it also forms coumarins and not chromones by changing the condensing agent for phosphorus pentoxide. Thus the

generalisation made by one of us (Chakravarti, *J. Indian Chem. Soc.*, 1932, **9**, 31) holds true in this case also.

In order to study the effects of substitutents in the acetoacetic ester molecule on the course of the reaction, 4-chlororesorcin has been condensed with different substituted acetoacetic esters *e.g.*, methylacetoacetic ester, ethylacetoacetic ester, propylacetoacetic ester, *iso*butylacetoacetic ester, benzylacetoacetic ester, α-chloroacetoacetic ester) and also with acetone dicarboxylic acid, aceto-succinic ester and benzoylacetic ester. These condense most readily with good yields forming coumarins in presence of sulphuric acid and even in presence of phosphorus pentoxide, as is proved by their mixed melting points and also by the identity of their derivatives. Thus it is found that a substituent in the acetoacetic ester molecule, however heavy or complex, does not in any way favour the formation of a chromone even in presence of phosphorus pentoxide contrary to the observations of Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 424). Incidentally it may also be mentioned that 4-chlororesorcin condenses with malic acid in presence of sulphuric acid to form 6-chloroumbelliferone in good yield just as resorcin produces under these conditions umbelliferone.

2-Nitroresorcin, prepared according to the method of Kauffmann and Pay (*Ber.*, 1904, **37**, 716) condenses with acetoacetic ester and methylacetoacetic ester to form coumarins (*e.g.*, 8-nitro-7-hydroxy-4-methylcoumarin and 8-nitro-7-hydroxy-3 : 4-dimethylcoumarin respectively). It has, however, not been possible to isolate any product using phosphorus pentoxide as the condensing agent due to the formation of resinous products

The introduction of a substituent in the acetoacetic ester molecule diminishes the yield of coumarin from 2-nitroresorcin and finally retards the reaction as shown below:

	Products.	Yield.
2-Nitroresorcin and acetoacetic ester	8-Nitro-7-hydroxy-4-methylcoumarin	60%
2-Nitroresorcin and methylacetoacetic ester	8 Nitro-7-hydroxy-3 :4-dimethylcoumarin	15
2-Nitroresorcin and ethyl-, propyl-or *iso*propylacetoacetic ester	No product isolated.	—

It is well known that umbelliferones exhibit violet fluorescence in alkaline solution. The chloroumbelliferones, described in this

paper, exhibit much stronger fluorescence (bluish violet) than umbelliferones, the fluorescence being appreciably increased with the introduction of heavier substituents in the pyrone ring. The fluorescence of umbelliferones is, however, completely destroyed by the presence of the nitro group.

Experimental.

Coumarins from 4-Chlororesorcin.

6-Chloro-7-hydroxycoumarin.—Chlororesorcin (4·5 g.) and malic acid (5 g.) were intimately mixed and heated carefully on a wire-gauge with double their weight of concentrated sulphuric acid (*d* 1·84); the mixture began to froth up in a few minutes and eventually appered as it were to solidify. Heating was continued until the liquid became clear. After cooling the solution was poured into water and the solid crystallised from glacial acetic acid as light ash-coloured needles or prisms, m.p. 271°, yield 1·5 g. It can be further purified by sublimation, when it is obtained as colourless prisms. It exhibits fluorescence in alkaline solution. (Found: Cl, 18·7. $C_9H_5O_3Cl$ requires Cl, 18·06 per cent).

The *acetyl* derivative, prepared by heating with acetic anhydride and fused sodium acetate, crystallised from dilute alcohol as colourless prisms, m.p. 166°. (Found: Cl, 14·7. $C_{11}H_7O_4Cl$ requires Cl, 14·85 per cent).

6-Chloro-7-hydroxy-4-methylcoumarin.—To a mixture of 4-chlororesorcin (4 g.) and acetoacetic ester (5 g.), cooled in ice, concentrated sulphuric acid (*d* 1·84, 10 c.c.) was slowly added with continuous shaking. The solution was kept overnight and poured into ice, when greenish solid separated. It was filtered and crystallised from glacial acetic acid (charcoal) as colourless prisms, m.p. 280°, yield 1·5 g. (Found: Cl, 16·03. $C_{10}H_7O_3Cl$ requires Cl, 16·8 per cent).

The *acetyl* derivative, prepared as usual by heating with acetic anhydride and fused sodium acetate, crystallised from dilute alcohol as colourless needles, m.p. 168°. (Found: Cl, 13·82. $C_{12}H_9O_4Cl$ requires Cl, 14·05 per cent).

The identical compound was obtained by using phosphorus pentoxide as the condensing agent. A mixture of 4-chlororesorcin (5 g.) and acetoacetic ester (5 g.) was heated on a boiling water-bath with phosphorus pentoxide (20 g.). After half an hour further amount of phosphorus pentoxide (20 g.) was again added and heating continued for 1½ hour. The mass was then cooled and treated with powdered

ice. The solid which separated was filtered and crystallised from glacial acetic acid (charcoal). The compound was found identical with that prepared by using concentrated sulphuric acid as condensing agent, m. p. 280°, mixed m. p. 280°.

The *acetyl* derivative, prepared in the usual way, melted at 168°, the m. p. being not depressed when mixed with the acetyl derivative of the compound prepared above using sulphuric acid.

The other compounds prepared are deseribed in the table.

Coumarins from 2-*Nitroresorcin.*

8-*Nitro*-7-*hydroxy*-4-*methylcoumarin.*—To a well-cooled mixture of 2-nitroresorcin (4 g.) and acetoacetic ester (5 c. c.) in a conical flask concentrated sulphuric acid (*d* 1·84, 8 c.c.) was gradually added. The solution was kept overnight and poured into ice, when yellow needles separated. These were filtrered, washed with water and crystallised from glacial acetic acid as yellow needles, m. p. 256° (decomp.). It is found to be identical with 8-nitro-7-hydroxy-4-methylcoumarin, prepared by Pechmann and Cohen (*Ber.*, 1901, **34**, 666) by nitrating β-methylumbelliferone, mixed m. p. 256° (decomp.). (Found : N, 6·4. Calc. for $C_{10}H_7O_5N$: N, 6·3 per cent).

The *acetyl* derivative, prepared by heating the substance with acetic anhydride and fused sodium acetate, crystallised from glacial acetic acid as yellow prisms, m. p. 198°.

The melting point of the acetyl derivative of Pechmann and Cohen's 8-nitro-7-hydroxy-4-methylcoumarin is recorded to be 165°. The compound, prepared according to Pechmann and Cohen (*loc, cit.*), was also acytylated with acetic anhydride and fused sodium acetate and it also melted at 198° and not at 165° as recorded by them. The acetyl derivative (m. p. 198°) has been deacetylated by hydrolysing with 20 % sulphuric acid and crystallised from glacial acetic acid, the deacetylated product melting at 256°.

8-*Nitro*-7-*hydroxy*-3 : 4-*dimethylcoumarin* —2-Nitroresorcin was condensed with methylacetoacetic ester in presence of concentrated sulphuric acid in the usual manner, It was crystallised from glacial acetic acid in yellow needles, m. p. 260° (decomp.). (Found : N, 6·7. $C_{11}H_9O_5N$ requires N, 6·4 per cent).

The acetyl derivative, prepared in the usual manner, crystallised from glacial acetic acid as yellow prisms, m.p. 246°. (Found : N, 5·47. $C_{13}H_{11}O_6N$ requires N, 5·1 per cent).

Name and formula.	Prepared from 4-chlororesorcin and	M. p.	Analysis. Found.	Req.	Remarks.
6-Chloro-7-hydroxy-3:4-dimethylcoumarin ($C_{11}H_9O_3Cl$)	Methylacetoacetic ester (using H_2SO_4 or P_2O_5).	248°	Cl, 14·78	15·3%	Colourless needles from glacial acetic acid.
The *acetyl* derivative ($C_{13}H_{11}O_4Cl$)	...	170°-71°	12·84	13·3	Silky needles from dilute alcohol.
6-Chloro-7-hydroxy-4-methyl-3-ethylcoumarin ($C_{12}H_{11}O_3Cl$)	Ethylacetoacetic ester (using H_2SO_4 or P_2O_5).	257-58°	14·91	14·9	Colourless needles from glacial acetic acid.
The *acetyl* derivative	...	145°	...	...	Colourless needles from dilute alcohol.
6-Chloro-7-hydroxy-4-methyl-3-propylcoumarin ($C_{13}H_{13}O_3Cl$)	Propylacetoacetic ester (using H_2SO_4 or P_2C_5).	230°	13·57	14·0	Yellow needles from glacial acetic acid.
The *acetyl* derivative ($C_{15}H_{15}O_4Cl$)	...	135°	11·91	12·0	Light yellow needles from dilute alcohol.
6-Chloro-7 hydroxy-4-methyl-3-*iso* butylcoumarin ($C_{14}H_{15}O_3Cl$)	*iso*Butylacetoacetic ester (using H_2SO_4).	199°	12·73	13·3	Colourless needles from glacial acetic acid.
6-Chloro-7-hydroxy-4 methyl-3-benzylcoumarin ($C_{17}H_{13}O_3Cl$)	Benzylacetoacetic ester (using H_2SO_4).	249°	11·91	11·64	Light yellow needles from glacial acetic acid.
3 :6-Dichloro-7-hydroxy-4-methylcoumarin ($C_{10}H_6O_3Cl_2$)	α-Chloroacetoacetic ester (using H_2SO_4 or P_2O_5).	254°	28·48	28·1	Crystallised from dilute alcohol. It exhibits bluish-green fluorescence.
The *acetyl* derivative ($C_{12}H_8O_4Cl_2$)	...	192°	24·82	24·73	Shining needles from dilute alcohol.
6-Chloro-7-hydroxycoumarin-4-acetic acid ($C_{11}H_7O_5Cl$)	Acetone dicarboxylic acid (using H_2SO_4).	210°	13·45	13·9	Needles from dilute alcohol. Purified by dissolving in $N/10$-Na_2CO_3 and acidification.
6-Chloro-7-hydroxy-4-methylcoumarin-3-acetic ester ($C_{14}H_{13}O_5Cl$)	Ethyl acetosuccinate (using H_2SO_4).	174°	10·92	11·9	Crystallised from dilute alcohol.
6-Chloro-7-hydroxy-4-phenylcoumarin ($C_{15}H_9O_3Cl$)	Benzoylacetic ester (using H_2SO_4).	258-260°	12·26	13·01	Colourless needles from glacial acetic acid.

Our grateful thanks are due to Prof. P. C. Mitter for placing the resources of his laboratory at our disposal.

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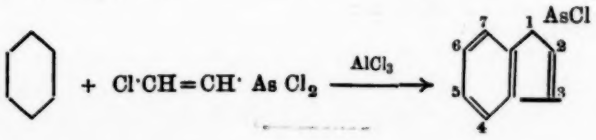
Received July 5, 1935.

Heterocyclic Compounds containing Arsenic in the Ring. A Preliminary Note.

By Hirendra Nath Das-Gupta.

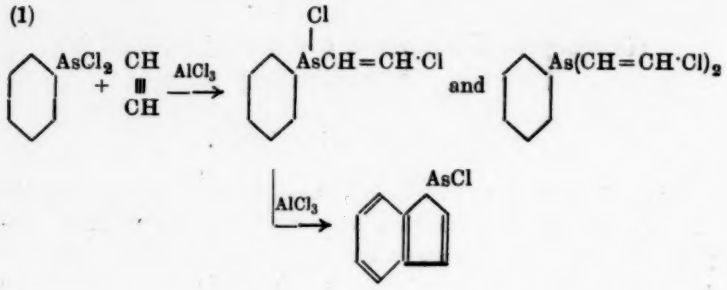
In the domain of organo-arsenic derivatives only a limited number of compounds are either isologous with hetero-nitrogenous ring compounds or in which arsenic takes part in the ring-formation. No compound is known which is isologous with indole. The present investigation was undertaken in November, 1933 with a view to prepare an arsenic analogue of indole. 1-Chloroarsindole was prepared by a direct method and the results of the same together with the procedures to be adopted towards establishing the correctness of the said formula were published (*Proc. Indian Science Congress*, 1933, p. 169). It appears that Mannich (*Arch. Pharm.*, 1935, **273**, 275) while studying the action of arsenic trichloride on 1-phenyl-1:3-diethylaminopropine, $Ph{\cdot}C \vdots C\,CH_2N{\cdot}Et_2$ to obtain $Ph{\cdot}CCl:C(AsCl_2)CH_2N{\cdot}Et_2$, analogous to the action of $AsCl_3$ on $Ph{\cdot}C \vdots CH$, got unexpectedly two different compounds, *viz.*, (*i*) $Cl-As{\cdot}C_4H_4{\cdot}CCl:C{\cdot}CH_2{\cdot}NEt_2$ and (*ii*) $Ph{\cdot}CCl:CH{\cdot}CH_2{\cdot}NEt_2$, HCl. The first compound was found to be isologous with indole and was accordingly designated as 2-(diethylaminomethyl)-1:3-dichloroarsindole and second one as the hydrochloride of 1-phenyl-1-chloro-3-diethylaminopropene. The author claims to be the pioneer in the synthesis of arsindole but probably through oversight he had not taken any note of the scheme of arsindole synthesis already published in 1933.

The chloroarsindole has been prepared by the present author by the action of β-chlorovinyldichloroarsine on pure benzene in the presence of anhydrous aluminium chloride as follows:



The formula assigned to chloroarsindole has been proved to be correct by the following syntheses: The experimental details will be communicated shortly.

(1)



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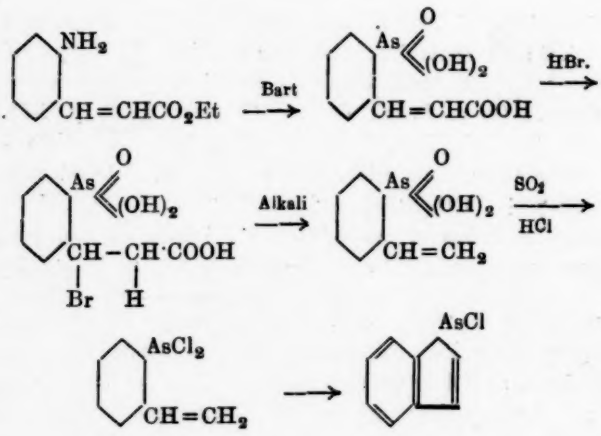

Compounds of the types $(C_6H_5 \cdot CH=CH)_2Hg$, $C_6H_5 \cdot CH=CH \cdot HgCl$ and $(C_6H_5 \cdot CH=CH)_3As$ have been prepared and attempts are being made to synthesise chloroarsindole from them.

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Received August 29, 1935.

The Phenylthiocarbamides. A Contribution to the Study of the Triad -N-C-S-. Part I. Aniline Thiocyanate.

By Hans Krall and Rameshwar Dayal Gupta.

Hofmann (*Compt. rend.*, 1858, **47**, 424) first prepared phenylthiocarbamide by the union of ammonia and phenyl mustard oil and called it 'thiosinamine de la série phénylique'. Schiff (*Annalen*, 1868, **148**, 338) prepared it by heating aniline and ammonium thiocyanate under reflux, presumably in aqueous solution, but published no details.

Clermont (*Compt. rend.*, 1876, **82**, 612) prepared it by the new classical method of evaporating together solutions of aniline hydrochloride and ammonium thiocyanate, heating the product for some hours at 100°, washing with water and crystallising from alcohol. Clearly he thought it to be formed by the isomerisation of the aniline thiocyanate transiently produced.

The latter salt is mentioned by Dixon and Hawthorne (*J. Chem. Soc.*, 1905, **87**, 468) as a bye-product of one of their reactions ; but nobody appears to have isolated it and studied its properties. Its preparation is not without difficulty. In an impure state it can be readily obtained in alcoholic solution by mixing alcoholic solutions of ammonium thiocyanate and aniline hydrochloride, filtering off the precipitated ammonium chloride and concentrating under reduced pressure in the cold. It is difficult to reduce the residual syrup to dryness without a vacuum so low that dissociative decomposition sets in ; also considerable chloride remains in solution and this cannot be precipitated by ether as the required salt is itself insoluble in that solvent.

It has also been obtained by the double decomposition in concentrated aqueous solution of calcium thiocyanate and aniline hydrochloride when the required aniline thiocyanate, although itself very soluble, crystallises out in preference to the other substances present. The yield under favourable conditions is about 30% of the theory, but the conditions have to be carefully controlled or various double compounds separate (*vide* Experimental). The best method consists in the direct union of aniline and thiocyanic acid in ether when a theoretical yield is obtained.

On heating it changes with evolution of heat into phenylthiocarbamide to the extent of 80%. At 85° this is complete within 30 minutes, at 110° in 15 minutes. Attempts to follow the change were not very successful, because the heat of reaction causes the temperature to rise rapidly with consequent acceleration of the change, also because the crystallisation of solid phenylthiocarbamide (m. p. 152°) from the melt sets in fortuitously and causes a further rise of temperature, and also because the presence of this solid makes the whole so pasty that samples cannot be removed for analysis.

At all temperatures some aniline thiocyanate remains unchanged suggesting an equilibrium such as has been established between thiocarbamide and ammonium thiocyanate (Reynolds and Werner, *J. Chem. Soc.*, 1903, **83**, 1), but on heating phenylthiocarbamide for four hours at 110° no reversion occurred.

Our results agree with the fact that it is never possible to obtain more than 80% of the theoretical yield in the classical method of preparation. In verifying that this is the case we have found that potassium thiocyanate in place of the ammonium salt does not affect the yield but gives a granular, and therefore more easily handled, product of heating ; we have also found that the two initial substances need only be mixed dry and heated at 110° for an hour instead of being evaporated in aqueous solution.

Experimental.

Isolation of aniline thiocyanate.—Thiocyanic acid was prepared by passing hydrogen sulphide through a suspension of mercuric thiocyanate in ether for 3-5 hours. This was filtered and 5-10 g. of the same salt added to take up excess of hydrogen sulphide. After 12 hours this was again filtered and estimated by Volhard's method.

A measured quantity was then slowly added to one equivalent of freshly distilled aniline in ether, when a heavy liquid separated which on cooling and vigorous stirring crystallised. Sometimes it was seeded with a previously prepared sample. The product was filtered at the pump and washed 10 to 12 times with dry ether. Colourless shining scales, m.p. 80-81°, yield theoretical. It is not appreciably hygroscopic but dissolves in a quarter of its weight of water or half its weight of alcohol and insoluble in ether or benzene ; its solution in water yields aniline with caustic soda solution, while titration with silver nitrate gave HSCN. (Found : S, 20·9, 21·0 ; HSCN, 38·7, 38·6. $C_6H_5NH_2$, HSCN requires S, 21·0 ; HSCN 38·8 per cent).

Interaction of aniline hydrochloride and calcium thiocyanate.—Aniline hydrochloride (65 g.) was dissolved in water (50 g.) by warming and the solution cooled to 50°; solid calcium thiocyanate (63 g.) was dissolved in this and the whole filtered. In cold weather the filtrate on standing deposited aniline thiocyanate (25 g., 30%), which was filtered off, drained at the pump and washed with ether. The mother liquor on standing for a couple of days deposited crystals of a quite different appearance which on examination proved to be a double thiocyanate of calcium and aniline. In warmer weather, however, the original solution deposited no crystals and when cooled in ice solidified to a moist mass (m. p. about 15-20°) from which no definite compound has so far been isolated. Treatment of this mass with ether resulted in a separation into three layers of which the middle one contained most of the substance. After repeated washing with ether it contained chloride, thiocyanate, aniline and calcium, probably in the equivalent-ratios of 1:3:2:2, but the total of these did not account for the total solid present; also some samples were found to undergo desulphurisation with alkaline lead solution, while complete miscibility with water precluded the presence of phenylthiocarbamide. Since the thiocyanates are well-known to have a tendency to form double compounds these observations would be of little interest but for the last which proves the presence of a substance freely soluble in water but having some of the properties of a thiocarbamide. Phenylthiocarbamide as ordinarily known is sparingly soluble in cold water (less than 1%) while aniline thiocyanate does not give the least trace of desulphurisation with alkaline lead solutions.

Evolution of heat on raising the temperature of aniline thiocyanate.—5 G. of samples were heated in baths of alcohol or toluene and a thermometer with its bulb in the melt read as follows:

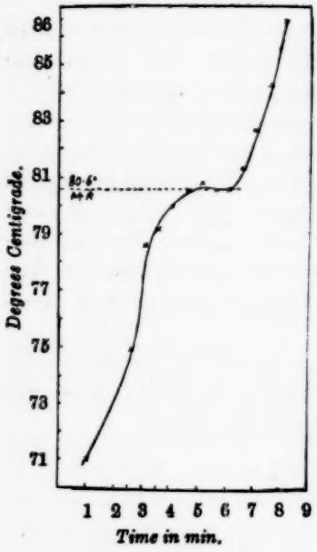
TABLE I.

Time after melting.	Temp. of bath.			Time after melting.	Temp. of bath.	
	110°	85°	78°		85°	78°
2 min.	124		79	42 min.	87	89
4	122		81	48	86	91
6	118	83	82	54	86	93
12	108	86	83	60	86	85
18		87	83	66	88	79
24		87	82	72	88	
36		87	79	78	86	

It will be seen that in all cases the temperature of the melt rose above that of the bath indicating some change with evolution of heat. In a bath of 110° the maximum was attained within 2 minutes, while at lower temperatures the change was naturally less sudden.

At lower temperatures there is usually a second maximum, as can be seen above which is not uniformly reproducible and gave us a lot of trouble until we found it to be simply due to the separation of solid phenylthiocarbamide (m.p. 152°) produced in the change.

These complications seem to render hopeless any attempt to determine the velocity of the change by following it analytically as has been done in the case of ammonium thiocyanate (Atkins and Werner, *J. Chem. Soc.*, 1912, **101**, 1172) where these difficulties do not seem to have been experienced.



Determination of m.p.—Since the determination of m. p. by ordinary methods cannot be relied upon owing to the occurrence of isomerisation, experiments were conducted similar to those in Table I, but paying attention to the period prior to melting. The results obtained in a bath of 86° are plotted in the diagram and it is clear that the melting point is 80° – 81°.

Heating causes isomerisation to the extent of about 80%.—A test tube containing about 5 g. was heated in a bath of boiling toluene (110°). Samples were removed after 1 and 3 hours respectively, extracted with about 100 c.c. of cold water, the soluble portion used for the determination of thiocyanate and the insoluble residue of phenylthiocarbamide dried at 100° and weighed. The same was done at 85°. Similar experiments were performed at 70° but as at this temperature the thiocyanate takes 40 minutes to melt, during which time isomerisation is going on, the test tube was in this case first

plunged in a bath of 85° to melt the mass (6 minutes), after which it was quickly transferred to the bath at 70°. The following results are typical.

TABLE II.

Result of heating aniline thiocyanate.

Duration of heating.	Product.	Temperature of bath. 110°	85°	70°
1 hr.	Phenylthiocarbamide	78%	80%	64%
	Aniline thiocyanate remaining	15	12	26
	Unaccounted for	7	8	10
2 hrs.	Phenyl thiocarbamide	77	83	77
	Aniline thiocyanate remaining	12	7	15
	Unaccounted for	11	10	8

Analytical procedure presented many difficulties not all of which have been surmounted. We have hitherto failed to discover a method of estimating thiocyanic acid in the presence of phenylthiocarbamide which can be relied upon under all conditions. This will form the subject of a subsequent communication.

Nevertheless the above figures can be relied upon to within one or two units and have been repeated many times without material variation. Continued heating at the lowest temperature results in further change in the same direction, but at the higher temperatures the change is essentially complete. Indeed secondary changes are beginning to set in even after one hour at 110°. No alteration of the conditions has enabled us to obtain more than 80-83% of phenylthiocarbamide.

This suggests the attainment of an equilibrium, but such an equilibrium between aniline thiocyanate and phenylthiocarbamide is difficult to understand as our experiments were all conducted at temperatures below the melting point of phenylthiocarbamide (152°) which does not revert to aniline thiocyanate under our conditions as is shown below. The fact that 8-10% is neither aniline thiocyanate, because it does not react with silver nitrate, nor phenyl-

thiocarbamide because it is soluble in a small quantity of cold water, is probably significant. Profound decomposition is unlikely at such moderate temperatures as 70° and 85°, nor is there any sublimation, smell or colour to suggest decomposition, and one is forced to the conclusion that a third isomeric body is present, a form of phenylthiocarbamide freely soluble in cold water. If this speculation should prove to be well-founded it would clear up several difficulties.*

The change of aniline thiocyanate to phenylthiocarbamide is not reversible.—(*a*) 5 G. of the substance heated for 4 hours at 110° were extracted with water but thiocyanate could not be detected even qualitatively.

(*b*) Equal parts of the two substances were heated for 2 hours at 110°. The melt was treated exactly as before. It proved to contain phenylthiocarbamide (90%) and aniline thiocyanate (5%). Comparison of these figures with those obtained by heating the thiocyanate alone show that the latter isomerises independently of the phenylthiocarbamide introduced. If the change were an ordinary reversible one, the results would be the same in both cases.

Summary.

1. Aniline thiocyanate has been isolated and examined.

2. Its isomerisation to phenylthiocarbamide, a change which has been taken for granted since 1846, has now been verified experimentally.

3. Isomerisation takes place over a wide range of temperature with considerable evolution of heat but never exceeds about 80% of the whole and some aniline thiocyanate always remains unchanged.

4. This suggests an equilibrium whereas up to 110° phenylthiocarbamide does not revert at a measurable rate.

5. This apparent equilibrium, the separation of aniline thiocyanate in liquid form during its preparation in ether, and results obtained by the interaction of aniline hydrochloride and calcium thiocyanate, indicate the existence of a third isomer hitherto unknown which undergoes desulphurisation with great ease but is freely soluble in cold water.

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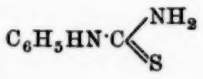
Received May 10, 1935.

* We have found that under very various conditions silver nitrate interacts with phenylthiocarbamide in the presence of nitric acid to the extent of 9-10% in excess of one equivalent.

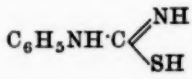
The Phenylthiocarbamides. A Contribution to the Study of the Triad -N-C-S-. Part II. Action of Hydrolytic Agents on Phenylthiocarbamide.

By Santsaran Mehta and Hans Krall.

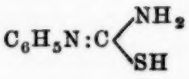
Phenylthiocarbamide may be expected to exist in one or more of the following forms: (*cf.* Werner, A new structural formula for thiocarbamide, *J. Chem. Soc.*, 1912, **101**, 2185; Krall, Constitution of guanidine, *J. Chem. Soc.*, 1915, **107**, 1398).



(I)



(II)



(III)

Hydrolysis provides an obvious line of attack on the problem of constitution, and might be expected to yield ammonia or aniline in varying proportions, with the simultaneous production of a compound having a hydroxyl group in place of the amino or anilino group. Experiments have shown, however, that this expectation is not realised, but that the hydrolytic reagent whether alkaline or acid produces decomposition of a dissociation type according to the following equations:—

$$C_6H_5NHCSNH_2 \longrightarrow H_2S + C_6H_5NHCN \quad \ldots \quad (i)$$

$$C_6H_5NHCSNH_2 \longrightarrow HCNS + C_6H_5NH_2 \quad \ldots \quad (ii)$$

$$C_6H_5NHCSNH_2 \longrightarrow NH_3 + C_6H_5NCS \quad \ldots \quad (iii)$$

In presence of a strong alkali changes (*i*) and (*ii*) occur simultaneously, but that represented by equation (*i*) largely predominates. With weaker alkalis changes (*i*) and (*ii*) still occur but that represented by equation (*ii*) increases at the expense of reaction (*i*). With water and weak acid, reaction (*i*) ceases altogether and (*ii*) predominates while the reaction represented by equation (*iii*) begins to be evident.

With strong acid changes (*ii*) and (*iii*) increase greatly (*cf.* the action of acetic anhydride on thiocarbanilide).

It is clear, therefore, that a progressive change in the *p*H value of the hydrolytic reagent causes a progressive change in the nature of the reaction and this may be due to a progressive tautomeric change in the constitution of phenylthiocarbamide. This will be discussed later.

In all cases varying but only small amounts of ammonia are produced and this is due to secondary changes such as the following:

$$HCNS + 2H_2O \longrightarrow CO_2 + H_2S + NH_3 \qquad (A)$$

$$C_6H_5NHCN + 2H_2O \longrightarrow CO_2 + C_6H_5NH_2 + NH_3 \qquad (B)$$

which we have verified under the conditions of our experiments. There is no doubt that ammonia appears as a primary product only in the presence of considerable concentrations of acid when the characteristic pungent smell of mustard oil also shows itself.

In certain cases small amounts of thiocarbanilide are also produced, and this too is undoubtedly due to secondary changes.

Experimental.

Action of concentrated alkali.—Phenylthiocarbamide (7·6 g.) and caustic potash (25 g.) dissolved in water (50 c.c.) were taken in a distilling flask connected to a receiver through a condenser. The receiver was connected to a Volhard trap. Steam was passed for 3-3½ hours and the distillate which was alkaline to litmus collected. The residual solution when cold was acidified with dilute acetic acid, copious evolution of hydrogen sulphide took place and a white precipitate of phenylcyanamide settled down.

The potassium sulphide from a similar experiment was determined by titration with alkaline zinc solution. [Found: H_2S, 1·39 g., *i.e.*, 81·7 % of theory as calculated from equation (*i*) above].

The alkalinity of the distillate calculated as ammonia gave NH_3=0·114 g. or 13·4 % of that calculated from equation (*iii*).

Evidently this change may be represented by the equation,

$$C_6H_5NHCSNH_2 \longrightarrow H_2S + C_6H_5NCNH.$$

the ammonia being due to secondary changes as already stated.

Action of N-*alkali and examination of volatile products.*—Phenylthiocarbamide (7·6 g.) and caustic potash (2·8 g.) dissolved in water (50 c.c.) were treated as in previous experiment. The distillate was now acidic. It was redistilled with caustic potash and the evolved ammonia collected in standard sulphuric acid. The residual solution in the distilling flask deposited crystals of unchanged phenylthiocarbamide and was further found to contain thiocyanic acid, alkali sulphide and very small amount of phenylcyanamide. From a similar experiment the amounts of thiocyanic acid and the alkali sulphide were determined. [Found: H_2S, 0·40 g. (23·53%); HCNS, 0·089 g. (3·31 %); NH_3, 0·16 g. (18·82%)].

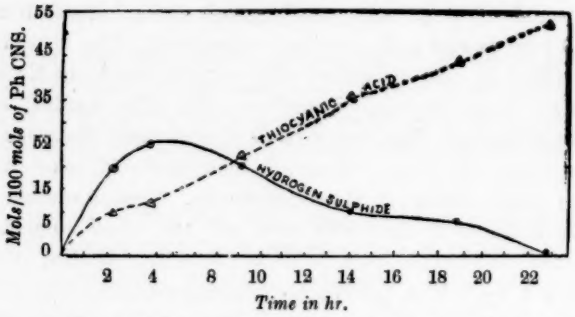
The estimation of thiocyanic acid in presence of hydrogen sulphide presented some difficulty. The procedure adopted was to acidify with dilute sulphuric acid, pass sulphur dioxide which within a minute or two decomposed the hydrogen sulphide in the cold; nitric acid then oxidised the excess of sulphur dioxide and the solution could be titrated with $N/10$-silver nitrate solution by Volhard's method.

Prolonged action of N-*alkali.*—Phenylthiocarbamide (30·4 g.) and caustic potash (11·2 g.) dissolved in water (200 c.c.) were refluxed and 5 g. samples were taken at intervals by means of a bucket formed from a length of silver wire and a small glass tube. The sample was cooled in a stoppered bottle, weighed and dissolved in water (25 c.c.), filtered from phenylthiocarbamide, etc., and the filtrate made up to 200 c.c. This procedure was rendered necessary by the fact that thiocyanic acid cannot be estimated in the presence of phenylthiocarbamide unless the quantity of the latter is small (separate communication). The amounts of hydrogen sulphide and thiocyanic acid were at once determined and their amounts in the total bulk of solution (*i.e.*, 241·6 g.) calculated. Thiocarbanilide was identified in small quantity and the smell of aniline was observed but no trace of mustard oil. The following results were obtained.

TABLE I.

Time.	Hydrogen sulphide.	Thiocyanic acid.
2 hours	19·61 %	10·14 %
4	28·04	11·64
8	20·81	22·51
13	11·71	35·99
18	8·69	44·05
22	1·31	52·0

FIG. 1.



These results in Table I and those plotted in Fig. 1 clearly indicate that the following two changes occur simultaneously:

$C_6H_5NH{\cdot}CSNH_2 \longrightarrow H_2S + C_6H_5NCNH.$

$C_6H_5NH{\cdot}CSNH_2 \longrightarrow HSCN + C_6H_5NH_2.$

The decline in the quantity of hydrogen sulphide after it has risen to a maximum remains unexplained.

Effect of varying amounts of caustic potash and of water alone.—Phenylthiocarbamide (5 g.) was refluxed with 1, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, 0 equivalent of caustic potash respectively dissolved in 132 c.c. of water, for 1 hour. The amounts of hydrogen sulphide and thiocyanic acid were estimated as before with the following results.

TABLE II.

Caustic potash.	Hydrogen sulphide.	Thiocyanic acid.
1 equiv.	23·20 %	5·7 %
1/2	8·67	6·8
1/4	2·29	7·0
1/8	0·86	7·9
1/16	Traces	8·7
0	Absent	8·81

This experiment shows that diminishing alkalinity favours the second change.

Action of barium hydroxide solution.—Phenylthiocarbamide (5 g.) was refluxed with 1 equivalent of barium hydroxide dissolved in 33 c.c. of water for an hour. The results obtained with one equivalent of caustic potash under identical conditions are given for comparison.

TABLE III.

Alkali.	Hydrogen sulphide.	Thiocyanic acid.
Barium hydroxide.	13·24 %	9·89 %
Caustic potash.	29·6	6·06

This experiment shows that a weaker alkali has the same effect as a more dilute alkali, *i.e.*, that the effects observed are due to the p_H values.

Action of acids.—Phenylthiocarbamide (5 g.) was heated under reflux with one equivalent of acid diluted with 50 c.c. of water for an hour. No trace of hydrogen sulphide was evolved. The percentage of thiocyanic acid was estimated. The results obtained are summed up in the following table.

TABLE IV.

Acid.	Hydrogen sulphide.	Thiocyanic acid.	Mustard oil.
Acetic	Nil	16·08 %	Faint smell.
Hydrochloric	Nil	61·85	Strong smell

SUMMARY.

1. Phenylthiocarbamide does not suffer hydrolysis of the normal type.

2. Hydrolytic agents produce decompositions of a dissociation type represented by the following equations:

$$C_6H_5NHCSNH_2 \longrightarrow H_2S + C_6H_5NH\,CN \qquad (i)$$
$$C_6H_5NHCSNH_2 \longrightarrow HCNS + C_6H_5NH_2 \qquad (ii)$$
$$C_6H_5NHCSNH_2 \longrightarrow NH_3 + C_6H_5NCS \qquad (iii)$$

3. Change No. (*i*) takes place only under alkaline conditions; (*ii*) occurs over a wide range but is favoured by increasing acidity; (*iii*) becomes appreciable only in the presence of strong acid.

4. In other words the carbon-sulphur bond is the first to be ruptured in the presence of alkali, the carbon-anilino in the presence of acids, the carbon-amine in the presence of the strongest acids.

Discussion of the bearing of these results on the problem of constitution is postponed pending the completion of further investigations now in progress.

Some of the above experiments were performed by Mr. G. V. Halwe, M.Sc.

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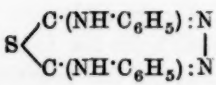
The Phenylthiocarbamides. A Contribution to the Study of the Triad -N-C-S-. Part III. Action of Nitrous Acid on Phenylthiocarbamide.

By Santsaran Mehta and Hans Krall.

Hagger and Doht (*Monatsh.*, 1906. **27**, 267) state that the chief product of the action of nitrous acid on phenylthiocarbamide is a base previously obtained by Hector (*Ber.*, 1889, **22**, 1176) by the action of 3% hydrogen peroxide on an alcoholic solution of phenylthiocarbamide, in presence of a few drops of hydrochloric acid. It has also been obtained by other workers from the action of various oxidising agents.

Hagger and Doht's paper is available to us in the form of an abstract only (*J. Chem. Soc.*, 1906, **90**, 577). It does not throw light on the constitution of phenylthiocarbamide, and does not state what acids were employed by the authors. It shows, however, that in acid solution nitrous acid behaves as an oxidising agent giving Hector's base



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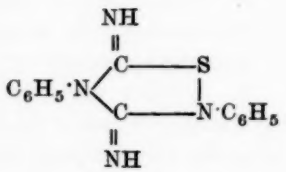


for which Hector (*loc. cit.*) has proposed the name dianilino-*o*-diazothiole or diphenyldiamido-*o*-diazothiole according to Widman's nomenclature (*J. pr. Chem.*, 1889, *ii*, **38**, 185). The constitution is open to doubt, the literature on the subject being conflicting.

The present investigation shows that in presence of hydrochloric acid mainly nitric oxide is evolved and the chief product of reaction is undoubtedly Hector's base, together with smaller amounts of phenyl mustard oil, phenyl *iso*cyanide and sulphur, but when acetic acid is employed mainly nitrogen is evolved and the chief product of reaction is phenylmustard oil together with very small amounts of Hector's

base, phenyl *iso*cyanide and sulphur. The following equations possibly represent the primary changes in the two cases:

$$2PhNHCSNH_2 + 4HNO_2 \rightarrow SC_{14}H_{12}N_4 + 4NO + 4H_2O + S \quad \ldots \quad (i)$$

$$PhNHCSNH_2 + HNO_2 \rightarrow PhNHCSOH \rightarrow PhNCS + N_2 + 2H_2O \quad (ii)$$

The oxidation change producing two molecules of nitric oxide and Hector's base results from the action of two molecules of nitrous acid on one of phenylthiocarbamide. The second which is a normal reaction of amines, producing one molecule of nitrogen and mustard oil, results from the action of one molecule of nitrous acid on one of phenylthiocarbamide. Since a clear idea of the progress of such interactions under different conditions can be ascertained by following the gas phase, experiments were carried out in the nitrometer, while in order to determine the yields of solid and liquid products formed separate experiments were conducted on a larger scale neglecting the gas phase.

The production of phenyl *iso*cyanide is not accounted for by any of these equations and is possibly produced by a different reaction; and besides smell no quantitative or qualitative tests could be employed as it is hydrolysed in acid medium as soon as formed. (Sidgwick, "Organic Chemistry of Nitrogen," 1910, p. 207.)

It is obvious from the facts just recorded that the action of nitrous acid on monophenylthiocarbamide proceeds on two different lines according as a strong or weak acid ioniser is present in the solution.

When one equivalent of pure sodium nitrite was gradually added to a solution of monophenylthiocarbamide in presence of excess of dilute hydrochloric acid, the insoluble yellow precipitate of the nitroso derivative of Hector's base settled at the bottom and in the solution was present Hector's base; much phenylthiocarbamide remained unacted upon and floated on the surface, together with a few drops of mustard oil. By adding a second equivalent of nitrite solution the unchanged phenylthiocarbamide was then acted upon and the same compounds were produced. The solution from the very start smelt of phenyl *iso*cyanide. The yield of Hector's base (including the corresponding amount of the base calculated from the quantity of the nitroso derivative formed) was 82-85% of that represented by equation (*i*) and the amount of mustard oil was about 10% of that represented by equation (*ii*). The composition of the evolved gas was 90·5% nitric oxide and 9·5% nitrogen.

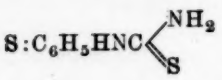
When, however, one equivalent of pure sodium nitrite was added gradually to a solution of phenylthiocarbamide in presence of excess of dilute acetic acid with constant and vigorous shaking, mustard oil was produced and in the solution was found a very small quantity of Hector's base, and the smell of phenyl *iso*cyanide was perceptible from the very start but disappeared towards the end of the reaction. In this case only a little phenylthiocarbamide remained unacted upon but when a second equivalent of nitrite was added it also underwent the change. Mustard oil was actually isolated to the extent of 66·5% of that represented by the equation

$$C_6H_5NHCSNH_2 + HNO_2 \longrightarrow C_6H_5NCS + N_2 + 2H_2O$$

and the amount of Hector's base was 23% of that required by the equation (*i*) The composition of the gas evolved was 80% nitrogen and 20% nitric oxide.

In order to arrive at a constitution which will account for the results obtained, the following facts will have to be kept in view.

(*i*) Since in presence of acetic acid, nitrogen is evolved the phenylthiocarbamide molecule must contain an amino group. It must, therefore, have one of the following configurations:



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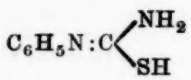

(*ii*) Since in presence of hydrochloric acid the change takes quite a different course, the configuration must be changed, and

(*iii*) Since no nitrogen is evolved during oxidation, no amino group is present.

(*iv*) During oxidation four hydrogen and one sulphur atoms are eliminated from two molecules of phenylthiocarbamide.

Experimental.

All gasometric experiments were made with the aid of Lunge's nitrometer or Allen's modification of it. The specimen of sodium nitrite used for the generation of nitrous acid contained 96·84% of sodium nitrite, a proportionate weight (71·25 : 69) corresponding with the theoretical required was used in each case. Each of the results

given below is a typical result selected from a number of experiments which did not differ by more than one unit per cent.

Action of Nitrous Acid on Phenylthiocarbamide in presence of a strong Acid.

Expt. 1. *In molecular proportion of* 1:1.—Preliminary experiments proved that the following was the most satisfactory method for carrying out the operation. 0·5 C.c. of ethyl alcohol was introduced into the apparatus and its level so adjusted by mercury reservoir that its major portion remained in the cup and communication between two portions of alcohol was kept through the hole in the stopper. Phenylthiocarbamide (0·076 g., *i.e.*, 1/2 mg. molecule) were tapped into the cup. The substance thus passed down into the nitrometer directly, and any particle remaining in the cup was then washed down into the apparatus by an additional half c c. of alcohol. 0·035625 G. (half mg. molecular proportion) of sodium nitrite dissolved in 2 c.c. of water were introduced into the apparatus, the cup was finally washed with 1 c.c. of water to wash in all traces of nitrite and then 2 c.c. of *N*-hydrochloric acid added. The tube was shaken to ensure complete reaction. Gas evolved 12·7 c.c. at 22·5° and 750 mm. mercury or 11·1 c.c. at N. T. P., *i.e.*, 22·2 c.c. from a mg. molecule and consisted of 9·5% nitrogen and 90·5% nitric oxide. (Theoretical volume 22·4 c.c. at N. T. P.) Under these conditions, therefore, the principal change is one of oxidation.

Expt. 2. *In molecular proportion of* 1:1, *on larger scale neglecting the gas phase.*—Phenylthiocarbamide (7·6 g.) and *N*-hydrochloric acid (200 c.c.) were taken in a litre beaker and 3·5625 g. of sodium nitrite dissolved in 500 c.c. of water were gradually added with constant stirring. The beaker was kept in a water-bath at a temperature of 20-21°. Heat was developed and the temperature reached 30°. Gas was evolved with great rapidity, the liquid which at first assumed a red colour quickly changed to pale yellow and the reaction was complete in about 30 minutes. The smell of phenyl*iso*cyanide developed from the very start and became almost intolerable by the end of the experiment; a deep yellow precipitate of the nitroso derivative of Hector's base settled at the bottom of the beaker with some sticky mass resembling sulphur. Practically half the phenylthiocarbamide together with a few drops of mustard oil floated at the top of the liquid.

The sticky mass was boiled with alcohol which deposited on cooling a very small amount of needle shaped crystals, m. p. 120-22°. The remainder was sulphur.

The mother liquor when made alkaline precipitated Hector's base, yield of Hector's base, 2·8 g; yield of sulphur, 0·3 g.

Expt. 3. *In molecular proportion of* 2:1 *in two stages.*—Expt. 1 was repeated and the evolved gas expelled from the nitrometer. 0·035625 G. of sodium nitrite dissolved in 5 c.c. of water was then added followed by 1 c.c. of *N*-hydrochloric acid. The evolution of gas was slower than with the first equivalent and 5 hours were required for the completion of the reaction.

Gas evolved with second equivalent 11·1 c.c. at 19·8° and 751 mm. or 10·18 c.c. at N. T. P. and contained 10·5% nitrogen and 89·5% of nitric oxide. Therefore total gas from both equivalents of nitrite is 21 28 c.c. at N. T. P., *i.e.*, 42·56 c.c. from a mg. molecule. The result, therefore, for the second equivalent is the same as for the first, half the thiocarbamide having evidently remained unchanged. In other words the change is mainly one of oxidation, two equivalents of nitrous acid being required as shown in equation (*i*). Further addition of nitrous acid gave no appreciable evolution of gas showing the action to be complete.

Expt. 4. *In molecular proportion of* 2:1 *on larger scale neglecting the gas phase.*—Expt. 2 was performed with the sole difference that two equivalents were used instead of one. The yields in this case were: yield of Hector's base, 5·3 g.; yield of sulphur, 0·6 g.; yield of mustard oil, few drops.

Action of Nitrous acid on Phenylthiocarbamide in presence of a weak acid.

Expt. 5. *In molecular proportion of* 1:1.—Phenylthiocarbamide (0·076 g.) were introduced in the nitrometer, 0·035625 g. ($\frac{1}{2}$ mg. molecular proportions) of sodium nitrite dissolved in 2 c.c. of water were introduced into the apparatus, the cup was finally washed with 1 c.c. of water to wash in all traces of nitrite and then 2 c.c. of *N*-acetic acid added. The tube was shaken from time to time. The reaction took 3 hours to complete being slower than in the presence of hydrochloric acid.

Gas evolved = 12·2 c.c. at 21·5° and 749 mm. or 11·15 c.c. at N. T. P. and contained 75·9% nitrogen and the rest was nitric oxide, *i.e.*, 22·3 c.c. from a mg. molecule.

Expt. 6. *In molecular proportion of* 1:1 *on larger scale and neglecting the gas phase.*—Phenylthiocarbamide (7·6 g.) and sodium nitrite (3·5625 g.) dissolved in 250 c.c. of water were taken in a litre flask and 200 c.c. of *N*-acetic acid were slowly added with constant stirring. The smell of *iso*cyanide was apparent from the very start, in the solution was present Hector's base (a test sample gave on warming with nitrite solution a yellow precipitate of nitroso derivative.) The liquid assumed a yellowish white colour and finally reddish brown, and as the reaction proceeded mustard oil settled at the bottom. No smell of *iso*cyanide could be detected towards the close of the reaction. Little thiocarbamide remained unacted. Yield of mustard oil, 2·5 g. (about 36%); yield of Hector's base (calculated from the amount of nitroso derivative) 1·5 g. (about 23%). Mustard oil was recovered from a similar experiment by steam distillation and the yield was 2·8 g. (*i.e.*, 41·5%).

The Hector's base underwent complex changes during steam distillation and was changed into a black resinous mass (1·4 g.), m. p. 88-89° and contained N and S. It dissolved in alcohol and chloroform with a blue fluorescence. All attempts to crystallise from the common solvents proved futile.

Expt. 7. *In molecular proportion of* 2:1 *in two stages.*—Expt. 5 was repeated and the evolved gas having been expelled from the nitrometer a second equivalent of nitrite was added and finally 1 c.c. of *N*-acetic acid. The gas was evolved very slowly and experiment took 2 hours to complete. Gas evolved=2·8 c.c. at 18° and 751 mm. or 2·6 c.c. at N. T. P., *i.e.*, 5·2 c.c. from 1 mg. molecule and was only nitrogen.

Therefore, the total gas from both stages (from a mg. molecule) was 27·5 c.c. at N. T. P. and contained 80% nitrogen and 20% nitric oxide and the oxidation change occurs at the beginning of the reaction. Thus unlike the corresponding case with hydrochloric acid (Expt. 3), the second equivalent gives a different result from the first.

Expt. 8. *In molecular proportion of* 5:4 *in one stage.*—The gas results in Expt. 7 indicated that the second equivalent of nitrous acid is more than required and that 4 equivalents of phenylthiocarbamide require 5 of nitrous acid for complete reaction. When these proportions were used these expectations were realised.

From ¼ mg. molecule the gas evolved was 15·1 c.c. at 18° and 751 mm. or 14·0 c.c. at N. T. P., *i.e.*, 28 c.c. from 1 mg. molecule, *i.e.*, the same quantity and composition as before.

Expt. 9. *In molecular proportion of* 5:4, *on larger scale and neglecting the gas phase.*—Phenylthiocarbamide (7·6 g.) and sodium nitrite (4·4531 g.) dissolved in water (300 c.c.) were taken in a litre flask and 200 c.c. of *N*-acetic acid added slowly with constant shaking. The changes were the same as in Expt. 8 and the yield of the products were: mustard oil, 4·4 g. Hector's base 1·5 g. Mustard oil recovered from a similar experiment by steam distillation was 4·5 g. (66·5%).

Summary.

(1) Nitrous acid reacts with phenylthiocarbamide in the presence of acids.

(2) In the presence of hydrochloric acid, about 90% of the phenylthiocarbamide interacts with two equivalents of nitrite solution being oxidised to Hector's base with evolution of nitric oxide, and the remaining 10% interacts with one equivalent producing phenyl mustard oil and nitrogen.

(3) In the presence of acetic acid the same two reactions occur but they exchange their relative importance. About 75% of the phenylthiocarbamide interacts with one equivalent of nitrite solution producing mustard oil and nitrogen and the remaining 25% requires two equivalents giving rise to Hector's base and nitric oxide.

(4) The oxidation change producing Hector's base and nitric oxide takes place first under any given conditions.

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Studies in the Camphor Series. Part I.

By Dines Chandra Sen.

In the present communication a general method of synthesis of cyclic thioketones has been described, by means of which thiocamphor has been synthesised in good yield. Thioborneol in quantity has also been obtained from thiocamphor by reduction.

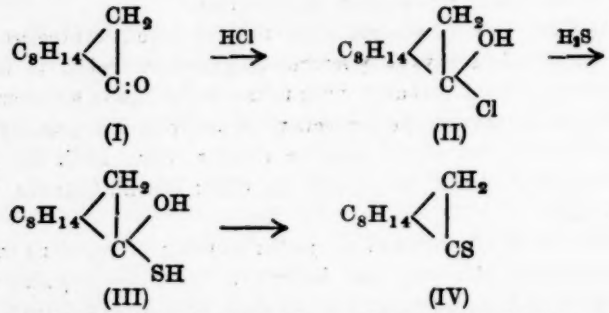
Attempts have been made from time to time to synthesise thiocamphor in various ways by several investigators who failed to isolate the pure compound, probably owing to the difficulties of its separation from the accompanying bye-products which are formed in quantity with a very small amount of thiocamphor (Wuyts, *Ber.*, 1903, **36**, 863; Houben and Doescher, *Ber.*, 1906, **39**, 3503; Rimini, *Gazzetta*, 1909, **39**, 11, 196).

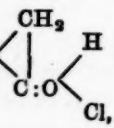
The chief disadvantage of the earlier methods of replacing oxygen by sulphur in aldehydes and ketones is that, the resulting thioaldehydes and thioketones in many cases polymerise to form trithioderivatives which have got very little chemical interests (*cf.* Barbaglia and Marquardt, *Ber.*, 1891, **24**, 1881; Rimini, *loc. cit*; Fromm and collaborators, *Ber.*, 1889, **22**, 2600; 1890, **23**, 60; Klinger, *ibid.*, 1877, **10**, 1877; Ruhemann, *J. Chem. Soc.*, 1905, **87**, 25). Fromm (*Ber.*, 1927, **60**, 2090) by passing a current of sulphuretted hydrogen and gaseous hydrochloric acid successively for several times in an alcoholic solution of cyclic ketones like *cyclo*hexanone and *cyclo*pentanone obtained tripolymerised thio derivatives. Mitra (*J. Indian Chem. Soc.*, 1931, **8**, 471; *ibid.*, 1933, **10**, 71) applied this reaction in the case of β-ketonic esters and obtained better results as he could isolate the nonpolymerised thio derivatives. This last method with sufficient modification (*vide* experimental), can be suitably applied for the preparation of thiocamphor in 50% yield.

It has been possible to synthesise, by the above method two stereoisomeric thio compunds, *racmic* and *laevo* varieties. The *dextro* variety has not yet been obtained. It has been observed that artificial or *r*-camphor as well as *l*-camphor yields *r*-thiocamphor (m. p. 145°) whereas the *d*-camphor when converted to thiocamphor yields the *l*-variety, m. p. 146°, $[\alpha]_D^{30°}$ −12° in 3·5% solution in ethyl acetate

in a tube of length 10 cm. The previous workers have recorded it as $[\alpha]_{D,}^{30} -44°$, in a solution of nearly the same strength. This anomaly cannot be decided till the *d*-variety is isolated. From the above experiments, it can only be assumed at this stage, that so far as optical activity is concerned, the *d*-thiocamphor is an unstable system compared to the *l*-variety, and the *d*-variety has a greater tendency to racemise than the *l*-variety.

The formation of thiocamphor probably takes place through an intermediate unstable hydrochloride and the mechanism can be expressed by the following scheme:—



An unstable hydrochloride of camphor easily decomposable by moisture, has been isolated (Shukoff and Kasatkin, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 137, 166), which to some extent supports this view. That thiocamphor cannot be prepared by means of sulphuretted hydrogen in presence of a moderate dehydrating agent like anhydrous sodium sulphate furnishes additional support to this view. As regards the constitution of camphor hydrochloride also, there are different views, for example, some describe it as a molecular compound $C_{10}H_{16}OHCl$, others as an oxonium compound  while others

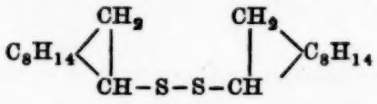
ascribe to it, the constitutional formula described above (II). From the constitutional formulæ of well-known additive compounds of ketones, *e.g.*, cyanhydrin, phosphoric acid derivatives, etc., the constitutional formula of this hydrochloride should be represented as in (II).

Regarding the constitution of thiocamphor, its direct synthesis from camphor shows that it is a thioketone formed simply by the

replacement of oxygen by means of sulphur. It forms phenylhydrazone, semicarbazone and oxime, which are identical with those of camphor as supported by their unchanged mixed melting points and analytical data. The behaviour of thioketones is thus analogous to that of ketones.

The slight difference between thiocamphor, thioborneol and dibornyl disulphide with respect to analytical data, does not prove conclusively, whether the substance isolated is pure thiocamphor. But the above reactions and molecular weight data and nearly the quantitative formation of semicarbazone prove conclusively that it is pure thiocamphor and not a disulphide. That it cannot form a yellow lead salt nor can it decolourise iodine solution prove that it does not contain thioborneol as an impurity.

Thioborneol has been prepared from thiocamphor by reduction with zinc and hydrochloric acid. The previous workers Wuyts, Rimini, etc. (*loc. cit.*) obtained thioborneol by decomposing the lead salt with acetic acid during which, evolution of sulphuretted hydrogen takes place and an impure substance is obtained whose m. p. is described by some workers as 50° and by others as 62-65°, whereas the m. p. observed by the present author is 120°. The above operation also diminishes the yield of thioborneol to a marked degree. A very small quantity of an oily liquid accompanies thioborneol and this lowers the m. p. to a considerable extent. Thioborneol forms dibornyl disulphide (A, m. p. 198°) by treatment with iodine in alcoholic solution.



(A)

Here also, the m. p. is found to be much higher than that described by the earlier workers (*cf.* Houben and Doescher, *loc. cit.*, m. p. 178°).

The above facts show that thiocamphor, thioborneol and their derivatives in the pure state were not known and the little study that has been made in this line also abounds in errors.

Experimental.

Preparation of thiocamphor.—Camphor (30 g.) in absolute alcohol (150 c. c.) was cooled to 0° and dry HCl gas and H_2S were passed

simultaneously for 5-6 hours. The solution changed from yellow, orange to deep red. The alcoholic solution was then treated with ice-cold water (25 c.c.) and the red precipitate was immediately filtered, as thiocamphor in the moist state is easily oxidisable. The precipitate was washed with dilute alcohol (1:1), then with a dilute solution of sodium bicarbonate and finally washed several times with water. The filtrate on further dilution gave more of the precipitate and this fractional precipitation is necessary, for, if camphor is precipitated along with thiocamphor it is very difficult to separate the two. The precipitate was then dissolved in benzene, the solution was dried over anhydrous sodium sulphate and benzene evaporated, when octahedral crystals separate from the concentrated solution, m. p. 145°, yield 15-16 g. The substance smells like camphor with a slightly sulphurous smell. It sublimes like camphor, is sparingly soluble in water and is readily soluble in common organic solvents. It is optically inactive. Like camphor it is acted upon by a chloroform solution of bromine and with sulphuric acid in presence of acetic anhydride. *l*-Camphor when similarly converted to thiocamphor gives the same racemic compound. [Found: C, 71·12; H, 9·6; S, 19·09. M. W. in benzene (cryoscopic), 167, 165. Calc. for $C_{10}H_{16}S$: C, 71·43; H, 9·52; S, 19·05 per cent. M. W., 168].

On subjecting *d*-camphor to the above treatment *l*-thiocamphor was obtained, m. p. 146°; $[\alpha]_D^{30}$ -12°, in a 3·5% ethyl acetate solution observed in a tube of length 10 cm. (Found: C, 71·18; H, 9·7; S, 19·1. Calc. for $C_{10}H_{16}S$: C, 71·43; H, 9·52; S, 19·05 per cent).

The phenylhydrazone—Thiocamphor (4 g.) was heated with phenylhydrazine (4 g.) on the water-bath till sulphuretted hydrogen was no longer evolved. The resulting product was dissolved in ether and the ethereal solution washed with a dilute solution of hydrochloric acid, dried over anhydrous sodium sulphate and distilled under reduced pressure, yield 3 g. It boils at 190°/10 mm. and at 230° (decomp.) under atmospheric pressure. It is identical with camphor-phenylhydrazone (*cf.* Balbiano, *Gazzetta*, 1885, **15**, 246; Wuyts, *loc. cit.*). (Found: C, 78·68; H, 9·22; M. W., 244·4. Calc. for $C_{16}H_{22}N_2$: C, 79·34; H, 9·1 per cent. M. W., 242).

The *oxime* was prepared as usual by refluxing for 2 hours an alcoholic solution of thiocamphor (5 g.), hydroxylamine hydrochloride (5 g.) and sodium acetate (7·5 g). It was crystallised from alcohol

as needle-shaped crystals, m. p. 118-19° (mixed m. p. with camphor oxime). (Found: N, 8·31. Calc. for $C_{10}H_{17}ON$: N, 8·38 per cent).

The *semicarbazone* crystallised from alcohol as needle shaped crystals, m. p. 237° (mixed m. p. with camphor semicarbazone). (Found: N, 20·12. Calc. for $C_{11}H_{19}ON_3$: N, 20·09 per cent).

Reduction of thiocamphor: Preparation of thioborneol.—This substance has been prepared by Wuyts, Rimini and others (*loc. cit.*), but the experimental details are not described. The action of zinc and acatic acid and also that of zinc and hydrochloric acid were tried, but in both cases, sulphuretted hydrogen was evolved during reduction, resulting in the formation of sulphur compounds of indefinite composition along with thioborneol. To the ice-cooled solution of thiocamphor (5 g.), in alcohol (25 c. c.), containing granulated zinc, an equal volume of a saturated solution of alcoholic hydrochloric acid was added and the solution kept overnight when the red colour was practically discharged, The reaction was allowed to take place finally for sometime at the ordinary temperature. Thioborneol was precipitated from the solution by means of ice-cold water and the product extracted with ether, dehydrated, and the ether evaporated. The solid was then dissolved in alcohol and treated with alcoholic solution of lead acetate when the insoluble lead salt of thioborneol separated out. The lead salt was suspended in alcohol and the lead removed as PbS. The thioborneol was precipitated from the alcoholic solution with water and extracted with ether, the ether distilled off, when a white solid with a small quantity of an oil separated out. On removing the oil on a porous plate the solid was crystallised as needles from ether, alcohol or petroleum ether, m. p. 120° (m. p. 61-62°, *cf.* Wuyts, *loc. cit.*). This also has camphoric smell sweeter than that of thiocamphor. It is soluble in common organic solvents. [Found: C, 70·74; H, 10·72; S, 18·81; M. W. in benzene (cryoscopic) 172·2. Calc. for $C_{10}H_{18}S$: C, 70·59; H, 10·59; S, 18·82 per cent. M. W., 170]. The yellow lead salt is fairly soluble in ether and can be crystallised from it as minute needles. [Found: S, 11·58. $Pb(C_{10}H_{17}S)_2$ requires S, 11·74 per cent].

Conversion of thioborneol to dibornyl disulphide.—Alcoholic solution of thioborneol (2 g.) was treated with an alcoholic solution of iodine till the brown colour became persistent and the excess of iodine was removed after 2 hours with sodium thiosulphate solution. The disulphide was precipitated by the addition of water and crystallised

from alcohol as needles, m. p. 198°, yield 1·8 g. It has slight camphoric smell. It is much less soluble than either thiocamphor or thioborneol. It is less sublimable than thiocamphor. [Found: C, 70·6; H, 10·3; S, 18·81; M. W. in benzene (cryoscopic), 335·6. Calc. for $C_{20}H_{34}S_2$: C, 71·01; H, 10·06; S, 18·93 per cent. M. W., 338]

In conclusion, my sincerest thanks are due to Sir P. C. Rây for his kind interest in the investigation and also for giving me facilities in his laboratory.

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The Formation of Amides from Nitriles by the Action of Hydrogen Peroxide.

BY L. MCMASTER AND C. R. NOLLER.

In a recent paper Murray and Cloke (*J. Amer. Chem. Soc.*, 1934, **56**, 2749) report the advantage of using a solvent such as methanol, ethanol or acetone in the Radziszewski reaction. The same conclusion was reached by us a few years ago during the course of a fairly detailed study of the optimum conditions for this reaction. Because of the inaccessibility of these data, it is thought desirable to briefly summarise them here.

In general, the hydrogen peroxide was added to a weighed portion of the nitrile and sufficient 95% ethanol added to bring the nitrile into solution. Sufficient 6*N*-sodium hydroxide was added to make the solution alkaline to litmus after which it was kept at 60° for 4 hours. If necessary, more sodium hydroxide was added during the course of the reaction to keep the mixture alkaline. The mixture was then cooled, neutralised with sulphuric acid, evaporated to dryness and either extracted with chloroform or crystallised from water. The amides were finally purified to constant melting point. In a few cases no ethanol was used but the nitrile was stirred with the hydrogen peroxide. The best conditions as determined by from two to eight experiments for each nitrile, using 3, 6, 12 and 30% hydrogen peroxide, are given in the following table.

Conditions and yields for the conversion of nitriles into amides by the action of hydrogen peroxide.

Nitrile.	Wt. of nitrile.	Amt. and conc. of H_2O_2.	Amt. of 95% C_2H_5OH.	Crude amide.	M.p. of purified amide (cor.).
Propio-	1·045 g.	10 c.c. 12%	None	49·6%	80·1°
n-Butyro-	1·050	20 6	None	64·9	114·6
n-Valero-	1·000	10 6	10 c.c.	62·5	104·1
*iso*Valero-	1·045	10 6	10	56·5	135·4
Phenylaceto-	1·095	20 6	20	59·5	159
Diphenylaceto-	1·000	5 30	10	69·0	166·5
α-Phenylcinnamo-	1·000	10 12	25	83·0	202·6
o-Nitrobenzo-	1·000	25 6	None	90·4	176·5
p-Nitrobenzo-	1·000	25 6	None	91·2	201·6
o-Tolu-	1·100	5 30	10	93·0	141·5
m-Tolu-	1·368	5 30	10	84·8	93·8
Piperonylo-	1·000	50 8	None	97·4	168·6
o-Nitropiperonylo-	0·500	10 12	None	85·4	199·6

The reaction with *o*-tolunitrile has been carried out on a much larger scale (88 g.) with equally satisfactory results ("Organic Syntheses," *Vol.* 13, p. 94).

It is of interest to note that the effect of alkali in this reaction is not merely to bring about a decomposition of the hydrogen peroxide in the presence of the amide, but that the hydroxyl ion is apparently a necessary catalyst for the reaction. Hydrogen peroxide in concentrations up to 30% when decomposed catalytically by manganese dioxide, freshly precipitated cobaltic hydroxide, cobaltic oxide or nickelic oxide, has no effect on neutral solutions of propionitrile or *o*-nitrobenzonitrile at temperatures up to 100°.

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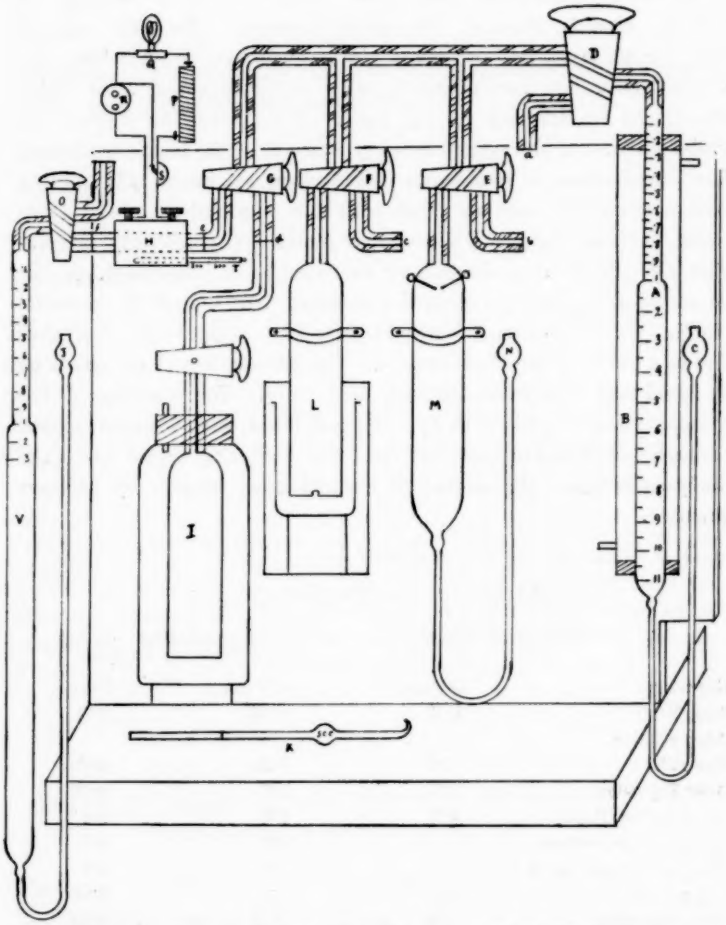
Note on a Routine Gas Analysis Apparatus.

By H. K. Sen, Kanailal Roy and Pankoj Roy.

The accurate and rapid analysis of gases where methane and hydrogen occur simultaneously, has been the subject of numerous contributions. For ordinary routine analysis, the explosion method is usually followed, but the composition of the explosive mixture, the shape of the explosion vessel, etc., play an important part in diminishing the accuracy of this method. Besides, methane is at times incompletely burnt, and any nitrogen that may be present is converted partially into nitrogen peroxide. The fractional combustion method is unquestionably superior, and, in fact, the most rational procedure for the estimation of a methane-hydrogen, or methane-hydrogen-carbon monoxide mixture.

The present communication arose out of an attempt to construct a gas analysis apparatus for class and research purposes, which could be depended upon, and which could be completed in a comparatively shorter time. Besides, it is extremely desirable that such an apparatus should be capable of being assembled in course of a few hours, and should be such that small volumes of gases of the order of 0·5 to 3 c.c. can be accurately analysed. It should be clearly stated in this connection that excepting the introduction of a vacuum creating system by a long tube (V), with a carefully graduated top, there is no substantially novel feature of the apparatus. This tube (V) which is provided with a good three-way stopper, capable of resisting good vacuum, serves as a Töpler pump for exhausting the volume of gas remaining in the tube containing the catalyst used for fractional combustion. The catalysts used are the ordinarily known ones, copper oxide, and palladium, but we have tried specially prepared manganese dioxide with satisfactory results.

A gas burette (A) is enclosed in a water-jacket (B) operated by a levelling pear (C). It is an 11 c.c. burette, made out of 10 c.c. and one c.c. pipettes, the latter being so graduated that 0·01 c.c. can be easily read. The two pieces are fused together and a correction for the junction is made by calibrating against a known volume. The burette ends in a three-way capillary stopper (D), to one end of which is fused an 1 mm. bore capillary tube, having two capillary limbs attached through two other three-way capillary



A—gas burette. B—water-jacket. C—levelling pear. D, E, F, G—three-way capillary stoppers. H—fractional combustion tube. I—bromine absorption apparatus. J and N—levelling pears. L—absorption pipette. M—explosion pipette. K—bent pipette for introducing absorbent liquids.

stop-cocks (E) and (F) as shown in the figure. A fourth three-way capillary stop-cock (G) serves for the connection with the fractional combustion tube (H) and the bromine absorption apparatus (I). The ends of the stop-cocks are connected to different absorption and washing systems. Glass to glass rubber connections can also be used without inaccuracy.

In the apparatus we have been using, the total volume of mercury used is 200 c.c. The copper catalyst tube (H) can be used for at least half a dozen times without regenerating the copper oxide, but the regeneration is easily effected after each experiment by drawing air by means of the pump-like system, VJ, whilst the rest of the system is being washed for the next experiment. The introduction of absorbents takes place by means of suitably bent pipettes (K) which are filled with the required absorbent to be blown carefully into the absorption pipette (L) without introducing air. If by any chance, an air bubble is introduced, it can be expelled by manipulating the levelling tube (N) of the explosion pipette (M). The tube V having a three-way stopper (O) can serve also as a gas burette, if necessary. The introduction of the gas to be analysed may take place through *a*, *b* or *c*. The washing of the system is conveniently done by a 5% sulphuric acid solution sucked through c from a Winchester bottle. The following actual results of analyses indicate the degree of concordance attainable by ordinary practice.

TABLE I.

Analysis of city illuminating gas.

	By explosion method	Fractional combustion method (CuO at 320° as catalyst)	
Gas taken	10·8 c.c.	10·5 c.c.	10·3 c.c.
After KOH	10·2	9·95	9·75
After alkaline Pyrogallol	9·9	9·65	9·45
After Br_2 water	9·5	9·3	9·05
After ammon. Cu_2Cl_2	8·6	8·4	8·2
After CuO-combustion		4·2	4·0
For explosion gas taken	4·4	3·0	2·8
Oxygen added	10·8	8·5	8·00
After explosion	8·38	6·65	6·20
After KOH	6·62	4·2	3·90
CO_2	5·55%	5·23%	5·34%
O_2	2·78%	2·85%	2·90%
Unsaturated	3·7%	3·33%	3·89%
CO	8·3%	8·57%	8·25%
H_2	39·8%	40·00%	40·77%
CH_4	31·85%	32·66%	31·84%
	91·96	92·64	92·99
Nitrogen	8·02	7·36	7·01
	100·00	100·00	100·00

TABLE II.

Analysis of a prepared mixture of Hydrogen and Methane (55 : 45), with palladium asbestos as catalyst.

Gas taken	3·10 c.c.	3·00 c.c.	0·9 c.c.
Oxygen added	8·10	7·00	3·12
After Pd.combustion	9·95	7·90	3·50
For explosion gas taken	9·6	7·3	3·15
After explosion	5·6	4·4	2·20
After KOH	4·25	3·15	1·88
H_2	55·6%	56·0%	55·5%
CH_4	45·10%	45·1%	45·5%
	100·70%	101·1%	101·00

Remarks—It would appear from these experiments that the hydrogen was not completely burnt in the palladium tube, as the contraction after explosion for methane was more than twice that of CO_2 formed. This was due to the fact that the Pd-tube was several times used before. When the tube is fresh, some methane is burnt, producing CO_2 and water. The CO_2 is first removed before proceeding with the explosion.

TABLE III.

Analysis of a prepared mixture of hydrogen and methane (70 : 30) with coarse copper oxide as catalyst.

H_2 ...	69·90%	69·82%	70·00%
CH_4 ...	30·10%	30·18%	30·00%
	100·00	100·00	100·00

Purity of electrolytic hydrogen from high pressure electrolyser — Volumes of hydrogen of the order of 0·78 c.c., 0·585 c.c., 0·64 c.c. as also 5·00 c.c. gave by the ordinary explosion method, contractions showing cent per cent purity. The same gas when passed over CuO-tube at 320°, is completely burnt, causing a rush of mercury to fill up the vacuum thus produced. To get a positive reading, dilution with inert gases is necessary.

TABLE IV

Test of the purity of electrolytic hydrogen from high pressure electrolyser.

Gas taken ...	0·78 c.c.	0·535 c.c	0·64 c.c.
Air added ...	3·60	2·50	2·56
After explosion	3·20	2·23	2·24
Contraction ...	1·18	0·805	0·96
H_2 ...	100·7%	100·2%	100%

The maintenance of a steady temperature of 310 to 320° is necessary to avoid a partial combustion of methane by the copper oxide method of fractional combustion, otherwise the results became erroneous.

The heating furnace employed to heat up the catalyst tube H, was built of nichrome wire wound round a porcelain tube as usual, embedded in a packing of ignited magnesia. The arrangement of the switch, S, permits of quick heating up of the furnace, by first leading the street current direct through the furnace, and of steady maintenance by leading the current through a by-pass of resistance. By substituting a silica tube for the glass, the higher temperature of 900° for the combustion of methane may also be attained, Such a furnace we have been using for the last three months almost daily for eight hours without any inconvenience. A coal gas analysis can be completed in half an hour by one who has got into the swing of the paths of the stop-cocks, and whose fingers have acquired delicate manipulative skill. It should be mentioned here that four to six passages, depending on the reactivity of the catalyst, are sufficient to complete the selective combustion of hydrogen. This portion of the operation does not occupy more than five minutes. If the CuO-catalyst is finely deposited on asbestos, the combustion of hydrogen begins visibly at 245° and is rapidly complete between 280° and 290°.

We take this opportunity of expressing our thanks to Mr. Sudhangsu Sekhar Ghosh, M.Sc., who was associated with one of us (H.K.S.) in the preliminary stage of the work.

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Studies in Indigoid Dyes.

By Sisir Kumar Guha.

In two previous papers (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 679; Guha and Basu-Mallik, *ibid.*, 1934, **11**, 395) it has been shown that 5-methyl-3-hydroxythionaphthene (Auwers and Arndt, *Ber.*, 1909, **42**, 551) interacts very readily with acenaphthenequinone, isatin and their various derivatives and also phenanthraquinone yielding beautiful indigoid vat dyes which impart a deeper shade on wool as well as on cotton than those of the corresponding compounds obtained from 3-hydroxythionaphthene (Bezdzik and Friedlander, *Monatsh.*, 1908, **29**, 376, 386; E.P. 6490-07; G.P. appl. G 25209; Dutt, *J. Indian Chem. Soc.*, 1932, **9**, 99; Guha, *ibid.*, 1932, **9**, 423).

In the present paper the action of 5-methyl-3-hydroxythionaphthene has been investigated on various aldehydes with the object of studying if the resulting products would possess any value as vat dyes. Benzylidene-2(5-methyl)-thionaphthene has been prepared and described by Auwers and Arndt (*loc. cit.*) but no dyeing property appears to have been examined and recorded. With the exception of this no other dyestuff has been obtained from 5-methyl-3-hydroxythionaphthene by condensation with aliphatic or aromatic aldehydes. The following aldehydes have, therefore, been condensed with 5-methyl-3-hydroxythionaphthene and the corresponding dyestuffs obtained: glyoxal, *p*-dimethylamino-, *m*-amino-, *p*-nitro-, *m*-nitro-, *p*-chloro-, *p*-methoxy-, *p*-hydroxy-, *m*-hydroxy-, *p*-methyl-, *m*-methoxy-*p*-hydroxybenzaldehyde, piperonal, protocatechuic and cinnamic aldehydes.

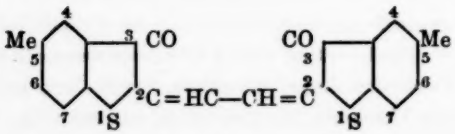
It has been found that the methylhydroxythionaphthene reacts quite easily with the above mentioned aldehydes. The condensation products are all coloured solids. They are characterised by their marked ability to crystallise so that they are quite suitable for the identification of aldehydes. In the case of nitro-, amino-, and hydroxybenzylidene-2-(5-methyl)-thionaphthenes it has been observed that the compounds having NO_2, NH_2 or OH group in the *meta* position to the benzylidene part of the molecule are lighter in shade than the corresponding substances having the same group in the *para* position. All these newly prepared substances dissolve in strong

sulphuric acid with a characteristic colour and the original substances are reprecipitated by the addition of water in a finely divided condition suitable for dyeing wool from an acid bath. The shades on wool are uniformly and fully developed. The atttempt to develop these colours on cotton from an alkaline hydrosulphite vat, except in the case of bis-2-(5-methyl)-thionaphthene-ethylene-indigo which gave very satisfactory result, was rather disappointing. Generally speaking, they offered great resistance to be converted easily into soluble vats. The shades obtained on cotton although fairly uniform, are invariably very much lighter than those of the original substances. Although repeatedly tried, the cinnamylidene compound could not, however, be developed on cotton.

Lastly, aceanthraquinone (Liebermann and Zsuffa, *Ber.*, 1911, **44**, 209) and the methylhydroxythionaphthene have yielded in boiling glacial acetic acid an indigoid dye, the dyeing properties of which have been compared with 2-(5-methyl)-thionaphthene-acenaphthylene-indigo (Guha, *loc. cit.*).

Experimental.

bis-2-(5-*Methyl*)-*thionaphthene-ethylene-indigo.*



An aqueous solution of glyoxal sodium bisulphite (0·284 g. in 5 c.c. of water) was added to a solution of 5-methyl-3-hydroxythionaphthene (0·328 g.) in hot absolute alcohol (25 c.c.) and the mixture treated with concentrated hydrochloric acid (5 c.c.) and shaken well. After 1½ hours' heating deep red fine silky needles separated which were filtered hot, washed with alcohol and then with hot water and crystallised from pyridine or nitrobenzene in clusters of dark red needles not melting below 300°. The dye is soluble in pyridine, nitrobenzene, aniline, xylene; difficultly soluble in amyl alcohol, chloroform, toluene; sparingly soluble in methyl alcohol, acetone; insoluble in petroleum ether, strong ammonia and caustic alkalis. It dissolves in strong sulphuric acid with a deep green colour and dyes wool in dark red shades; and cotton is dyed in beautiful violet-red

shade from a deep yellow vat. (Found: S, 18·6. $C_{20}H_{14}O_2S_2$ requires S, 18·28 per cent).

4′-Dimethylaminobenzylidene-2-(5-methyl)-thionaphthene.

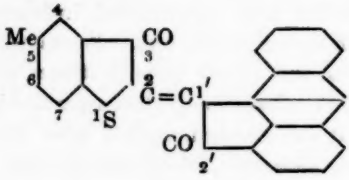
A solution of 5-methyl-3-hydroxythionaphthene (0·328 g.) and p-dimethylaminobenzaldehyde (0·298 g.) in hot absolute alcohol (10 c.c.) on treatment with concentrated hydrochloric acid (1 c.c.) turned deep reddish brown (almost red). It was heated on the water-bath for 15 minutes and cooled under a stream of water when the hydrochloride of the condensation product separated in yellow diamond-shaped crystals. It was collected, washed with dilute alcohol (1:1) when the free base separated, which was collected, washed well with hot water and crystallised from dilute acetic acid or pyridine in shining red prisms, m.p. 198-99°. It is soluble in acetic acid, chloroform, methyl alcohol, ethyl alcohol, amyl alcohol, pyridine, nitrobenzene, aniline, benzene, toluene, xylene, acetone, carbon tetrachloride; sparingly soluble in petroleum ether, insoluble in ammonia and caustic alkalis. Strong sulphuric acid dissolves it with a blue colouration. It dyes wool in cinnabar-red shades and cotton in pink colour from faintly red vat. (Found: N, 4·98. $C_{18}H_{17}ONS$ requires N, 4·74 per cent).

3′-Aminobenzylidene-2-(5-methyl)-thionaphthene.—The hydrochloride separated as yellow shining plates on heating for 15 minutes the reddish brown solution obtained by adding methylhydroxythionaphthene (0·656 g.) in 8 c.c. of boiling alcohol to *m*-aminobenzaldehyde (0·484 g.) in a mixture of boiling alcohol (30 c.c.) and concentrated hydrochloric acid (5 c.c.). It was collected and boiled with 2*N*-caustic soda, filtered hot and washed with hot water and crystallised from dilute pyridine in brownish yellow silky needles, m.p. 157°. The substance gives a violet-blue solution in strong sulphuric acid and dyes wool in deep yellow shades from an acid bath and cotton in yellow shades from an alkaline faintly yellow vat. All other properties resemble those of the preceding compound. (Found: N, 5·58. $C_{16}H_{13}ONS$ requires N, 5·24 per cent).

The compounds described in Table I were prepared by taking molecular quantities of 5-methyl-3-hydroxythionaphthene and the corresponding aldehyde in hot absolute alcohol and adding 2-3 c.c. of concentrated hydrochloric acid The product separated at once from the boiling solution. It was collected and crystallised from dilute

acetic acid except where otherwise mentioned. They are soluble in nitrobenzene, aniline, pyridine, amyl alcohol, acetic acid and all of them except the hydroxy compounds are insoluble in strong ammonia and caustic alkalis.

2-(5-Methyl)-thionaphthene-1'-aceanthrylene-indigo.



5-Methyl-3-hydroxythionaphthene (0·328 g.) was added to a solution of aceanthraquinone (0·464 g.) in boiling acetic acid (40 c.c.) and heated for a while. The whole solution turned deep reddish brown and on the addition of concentrated hydrochloric acid (2 c.c.) a deep red crystalline substance was at once precipitated. The mixture was heated to boiling for 15 minutes and filtered hot, the product washed well with glacial acetic acid and boiled water, dried and crystallised from xylene or nitrobenzene in fine clusters of deep red needles, m.p. above 310°, on further heating it volatilises evolving red vapours. It is soluble in pyridine, nitrobenzene, aniline, xylene; difficultly soluble in amyl alcohol, benzene, toluene, chloroform; sparingly soluble in alcohol, petroleum ether; moderately soluble in acetic acid, acetone, carbon tetrachloride. The solution in concentrated sulphuric acid is yellowish green. It dyes wool in orange-brown shades from an acid bath and cotton in light red ochre colour from a yellow vat. (Found: S, 8·45. $C_{25}H_{14}O_2S$ requires S, 8·46 per cent).

TABLE I.

B = Benzylidene; C = Cinnamylidene; P = Piperonylidene; M = 2-(5-Methyl)-thionaphthene.

Name and formula.	M.p.	Colour in strong H_2SO_4	Shade on wool from acid bath.	Shade on cotton. Colour of vat in brackets.	Analysis. Found.	Calc.	Remarks.
4'-Nitro-BM $C_{18}H_{11}O_3NS$	264°	Greenish blue	Orange-yellow	Light orange (deep orange-red)	N, 5·03	4·71	Orange-red rectangles from glacial acetic acid, soluble in chloroform, benzene, toluene, xylene; moderately soluble in CCl_4, acetone; sparingly soluble in ethyl alcohol, petroleum ether.
3'-Nitro-BM $C_{18}H_{11}O_3NS$	233°	Blue	Yellow	Yellow (light yellow)	N, 4·99	4·71	Yellow silky rectangles from acetic acid; solubilities same as in the previous compound.
4'-Chloro-BM $C_{18}H_{11}OClS$	178°	Reddish brown	Yellow	Faint yellow (faint greenish yellow)	Cl, 12·54	12·38	Bright yellow rectangles from alcohol, soluble in $CHCl_3$, alcohol, benzene, xylene, acetone, CCl_4; sparingly in petroleum ether.
4' Methoxy-BM $C_{17}H_{14}O_2S$	157°	Deep red	Bright yellow	Yellow (faint yellow)	S, 11·08	11·34	Bright yellow needles, moderately soluble in petroleum ether; other properties resemble the preceding compound.
4'-Hydroxy-BM $C_{16}H_{12}O_2S$	252°	Brownish red	Deep and bright yellow.	Yellow (colourless)	12·27	11·94	Light brownish yellow silky needles, soluble in methyl alcohol, ethyl alcohol, acetone, toluene, xylene; difficultly soluble in $CHCl_3$ and benzene.
3'-Hydroxy-BM (separated on cooling) $C_{16}H_{12}O_2S$	200°	,,	Deep yellow	Faint yellow (colourless)	12·20	11·94	Deep yellow needles, soluble in alcohol, chloroform, benzene, toluene, xylene, difficultly in CCl_4.

Name and formula.	M.p.	Colour in strong H_2SO_4.	Shade on wool from acid bath.	Shade on cotton. Colour of vat in brackets.	Analysis. Found.	Calc.	Remarks.
4′-Methyl-BM. (Separated on cooling) $C_{17}H_{14}OS$	159°	Brownish red	Yellow	Yellow (faint yellow)	S, 12·09	12·03	Yellow clusters of needles from glacial acetic acid, soluble in acetone, $CHCl_3$, COl_4, benzene, toluene, xylene, petroleum ether; difficultly in methyl and ethyl alcohol.
3′-Methoxy-4′-hydroxy-BM (Do.) $C_{17}H_{14}O_3S$	194°	Deep red	Deep yellow	Yellowish brown (pinkish red).	10·6	10·73	Deep yellow needles, soluble in alcohol, $CHCl_3$, benzene xylene, acetone, CCl_4.
3′:4′-Dihydroxy-BM. $C_{16}H_{12}O_3S$	248°	,,	Brownish yellow	Light reddish brown (light blue)	11·46	11·26	Light brown shining rectangles, soluble in methyl alcohol, ethyl alcohol. acetone; moderately in $CHCl_3$, benzene, xylene; insoluble in petroleum ether.
P M $C_{17}H_{12}O_3S$	231°	Purple	Deep yellow	Dull faint yellow (faint yellow)	11·05	10·81	Deep yellow needles, soluble in acetone, $CHCl_3$, benzene; difficultly in alcohol; sparingly in petroleum ether.
C M $C_{18}H_{14}OS$	184°	Violet-red	Dull orange-yellow.		11·26	11·51	Orange-yellow small needles, soluble in acetone, $CHCl_3$, benzene xylene, alcohol; sparingly in petroleum ether.
BM (*cf.* Auwers & Arndt, *loc.cit.*) $C_{16}H_{12}OS$	147°	Brownish red	Yellow	Light yellow (faint yellow)	12·49	12·69	Yellow shining rectangles, soluble in acetone, CCl_4, methyl alcohol, benzene, toluene. xylene; moderately soluble in petroleum ether.

My grateful thanks are due to Dr. K. S. Caldwell for encouraging me during the progress of this work.

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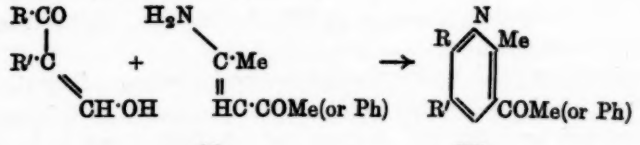
Synthesis in the Pyridine Series. Part II.

By Umaprasanna Basu and Basudeb Banerjee.

It has been observed by Mumm and Böhme (*Ber.*, 1921, **54**, 726) that though pyridines are readily obtained by reacting ethyl β-aminocrotonate with acyl pyruvic esters, the former fails to give pyridines when condensed with β-diketones or hydroxymethylene ketones. Contrary to this observation, one of us (Basu, *J. Indian Chem. Soc.*, 1935, **12**, 289) has recently shown that the crotonic acid derivative readily condenses with hydroxymethylene ketones to give rise to various pyridine-β-carboxylates. Further as acetylacetoneamine, benzoylacetoneamine and diacetonitrile have also been found to react with hydroxymethylene-*cyclo*hexanone to afford the formation of various *Bz*-tetrahydroquinoline derivatives (*cf.* Basu, *Annalen*, 1935, **514**, 292), the above reaction might be considered to be a general one and consequently could be carried out with any tautomeric compound of the ketimine-enamine type on the one hand and a hydroxymethylene ketone on the other. With a view to establish the validity of the above statement and at the same time to find out a direct method for the synthesis of β-pyridylketones, the present investigation was mainly undertaken. It has now been found that ammonia derivative of acetylacetone, or that of benzoylacetone readily reacts with a hydroxymethylene ketone (I) to give rise to the pyridyl derivative (II) according to the scheme:



(I) (II)

where R = alkyl or aryl group and R′ = H or alkyl group.

Thus, on heating an equimolecular mixture of acetylacetoneamine and hydroxymethylene acetophenone in ethereal solution on a water-bath for several hours, 2-methyl-6-phenyl-3-acetylpyridine (II, R = Ph, R′ = H) was isolated from the reaction mixture by first extracting

it with dilute hydrochloric acid and then neutralising the acid extract with sodium carbonate. Similarly the above amine gave 2-methyl-6-*p*-tolyl- and 2:5-dimethyl-6-ethyl-3-acetylpyridines when reacted respectively with hydroxymethylene methyl-*p* tolylketone and hydroxymethylene derivative of diethylketone. The corresponding 3-benzoylpyridines were again obtained by condensing the above hydroxymethylene ketones with benzoylacetoneamine.

All the β-pyridylketones described in the present paper are usually low melting colourless solids which are sparingly soluble in water but readily dissolve in ether, alcohol and other common organic solvents. They are tertiary bases and readily form hydrochlorides. In acid solution they give double salts with mercuric chloride and in alcoholic solution picrates with picric acid. The phenylketones differ from the methyl analogues with respect to their reactivity towards semicarbazide, as the former does not react whereas the latter readily gives the semicarbazones.

Certain pyridine bases, *e.g.*, 2:5:6-trimethyl-, 2:5-dimethyl-6-ethyl-, 2-methyl-6-*p*-tolylpyridines, have also been synthesised for the first time by lime distillation of their 3-carboxylic acids obtained in their turn by hydrolysing the respective condensation products of ethyl β-aminocrotonate with hydroxymethylene methylethylketone, hydroxymethylene diethylketone and hydroxymethylene methyl-*p*-tolylketone.

Experimental.

Acetyl Acetoneamine.

This was prepared by passing ammonia to acetylacetone according to Combes and Combes (*Bull. Soc. chim.*, 1893, *iii*, **7**, 778) and obtained as a refracting liquid, b. p. 92°/14 mm. On cooling it set to a crystalline mass.

Condensation with hydroxymethylene acetophenone: Formation of 2-methyl-6-phenyl-3-acetylpyridine.—The hydroxymethylene ketone was prepared according to the method of Büllow and Sicherer (*Ber.*, 1901, **34**, 3891) and was preserved as its copper salt. It was freshly liberated from the above salt before use and was taken in ether. The ethereal solution was then heated under reflux with the required molecular quantity of acetylacetoneamine for about 16 hours. The solution became turbid owing to the separation of water. It was extracted with dilute hydrochloric acid (12 %) and the acid extract was

neutralised with sodium carbonate when the pyridine ketone slowly separated out as a low-melting solid. On crystallisation from dilute alcohol it melted at 90°, yield 50%. (Found: N, 6·75. $C_{14}H_{13}ON$ requires N, 6·63 per cent).

The pyridine ketone is insoluble in water, difficultly soluble in petroleum ether but easily dissolves in ether, alcohol and other common organic solvents.

The *hydrochloride*.—The base was dissolved in the minimum quantity of dilute hydrochloric acid (12 %) by warming, when on cooling crystals of the hydrochloride of 2-methyl-6-phenyl-3-acetylpyridine separated out, m.p. 143-44°. (Found: Cl, 14·30. $C_{14}H_{13}ON$, HCl requires Cl, 14·34 per cent).

The *picrate*.—The ketonic base was heated with an alcoholic solution of picric acid for a few minutes when on dilution with water the picrate of the base separated out. On recrystallisation from alcohol it was obtained in shining yellow prismatic needles, m.p. 166°. (Found: N, 12·60. $C_{20}H_{16}O_8N_4$ requires N, 12·72 per cent).

The *semicarbazone*.—A solution of semicarbazide hydrochloride on being neutralised with ammonia, was mixed with an alcoholic solution of the pyridine ketone. This was then heated under reflux on a water-bath for about $2\frac{1}{2}$ hours ; on dilution with water the semicarbazone of the acetylpyridine derivative separated out and was recrystallised from alcohol as long rectangular prisms, m.p. 212°. (Found: N, 21·19. $C_{15}H_{16}ON_4$ requires N, 20·89 per cent).

The *oxime*.—A solution of hydroxylamine hydrochloride was neutralised with ammonia and heated with an alcoholic solution of the pyridine ketone for more than 5 hours on a water-bath. On diluting the reaction mixture with water, the oxime separated, which was obtained in microscopic needles from dilute alcohol, m.p. 106°. (Found: N, 12·62. $C_{14}H_{14}ON_2$ requires N, 12·38 per cent).

*Condensation with hydroxymethylene methyl-*p*-tolylketone: Formation of 2-methyl-6-*p*-tolyl-3-acetylpyridine*.—The hydroxymethylene compound, prepared by the method of Benary, Meyer and Charisius (*Ber.*, 1926, **59**, 108) was preserved as its sodium salt. An ethereal solution containing the molecular quantities of acetylacetoneamine and the above hydroxymethylene ketone, freshly liberated from its sodium salt, was refluxed for about 16 hours as in the previous case. On extracting the ethereal solution with dilute hydrochloric acid and neutralising the acid extract with sodium carbonate, the acetylpyridine derivative was isolated. It crystallised from dilute

alcohol in clusters of needles, melting at 78°. (Found: N, 6·34. $C_{15}H_{15}ON$ requires N, 6·20 per cent).

The *hydrochloride*, melts at 150-51°. (Found: Cl, 13·51. $C_{15}H_{15}ON$, HCl requires Cl, 13·58 per cent).

The *picrate* separated as yellow needles from alcohol, m.p. 163-64°. (Found: N, 11·49. $C_{21}H_{18}O_8N_4$ requires N, 11·89 per cent).

The *semicarbazone* was obtained as small needles from alcohol, m.p. 207°. (Found: N, 20·21. $C_{16}H_{18}ON_4$ requires N, 19·85 per cent).

The *oxime* separated as long shining needles from alcohol, m.p. 127°. (Found: N, 11·3. $C_{15}H_{16}ON_2$ requires N, 11·60 per cent).

Condensation of hydroxymethylene diethylketone: Formation of 2:5-dimethyl-6-ethyl-3-acetylpyridine.—An ethereal solution of hydroxymethylene derivative (11·3 g.), prepared according to the method of Claisen and Meyerowitz (*Ber.*, 1899, **32**, 3275), and acetylacetoneamine (9·8 g.) were heated under reflux as usual. On subsequent treatment of the reaction mixture, about 8 g. of the pyridine derivative were obtained, which when crystallised from boiling water melted at 60°. (Found: N, 7·97. $C_{11}H_{15}ON$ requires N, 7·90 per cent).

The *picrate* was obtained as yellow rhombic crystals, m.p. 118°. (Found: N, 13·99. $C_{17}H_{18}O_8N_4$ requires N, 13·79 per cent).

The *semicarbazone* crystallised from alcohol in rectangular prisms, m.p. 201°. (Found: N, 24·29. $C_{12}H_{18}ON_4$ requires N, 23·90 per cent).

The *oxime* crystallised from alcohol (50%) in rectangular prisms, m.p. 128°. (Found: N, 14·96. $C_{11}H_{16}ON_2$ requires N, 14·58 per cent).

Benzoylacetoneamine.

The amine was prepared according to the method of Knoevenagel (*Ber.*, 1903, **36**, 2188) by passing ammonia to an alcoholic solution of benzoylacetone and was obtained in shining rhombic crystals, m.p. 143°.

Condensation with hydroxymethylene acetophenone: Formation of 2-methyl-6-phenyl-3-benzoylpyridine.—An ethereal solution of the hydroxymethylene ketone, freshly liberated from its sodium salt (10 g.), was mixed with an alcoholic solution of benzoylacetoneamine (8 g.) and the mixture was heated under reflux for more than 15 hours. The solution was then concentrated and treated with dilute hydrochloric acid (12%). The acid solution was filtered and the filtrate was

neutralised with sodium carbonate, when an oil was obtained. This was dissolved in ether and the ethereal solution was shaken with dilute hydrochloric acid. The acid extract was again neutralised with soda ; when a solid separated out which crystallised from alcohol in prismatic plates, m.p. 77°. (Found: N, 5·25. $C_{19}H_{15}ON$ requires N, 5·13 per cent). It is soluble in ether, alcohol, etc., but insoluble in water. On heating with an alcoholic solution of picric acid the substance gave a picrate as tiny needles, m.p. 196° after crystallisation from alcohol. (Found: N, 11·29. $C_{25}H_{18}O_8N_4$ requires N, 11·15 per cent). The phenylpyridineketone did not give any semicarbazone under the usual conditions.

Condensation with hydroxymethylene methyl-p-tolylketone: Formation of 2-methyl-6-p-tolyl-3-benzoylpyridine.—An equimolecular mixture of the above hydroxymethylene ketone and benzoylacetoneamine was heated in ether-alcoholic solution as in the previous case. On subsequent treatment the benzoylpyridine was easily isolated and was obtained in fine prisms after crystallisation from alcohol, m.p. 84°. (Found: N, 5·11. $C_{20}H_{17}ON$ requires N, 4·88 per cent). Its *picrate* has already been described (*cf.* Basu, *J. Indian Chem. Soc.*, 1935, **12**, 289).

Ethyl β-Aminocrotonate.

Condensation with hydroxymethylene diethylketone: Formation of ethyl 2:5-dimethyl-6-ethylpyridine-3-carboxylate.—The hydroxymethylene derivative (17·0 g.) and the aminocrotonate (19·0 g.) in ethereal solution were heated under reflux for 15 hours. The reaction mixture on usual treatment, gave an oil (12·0 g.) which distilled at 145°/10 mm. (Found: N, 6·54. $C_{12}H_{17}O_2N$ requires N, 6·76 per cent).

It is a yellow refracting liquid, refractive index being 1·0005 at 39°. It is sparingly soluble in water but is easily miscible with all common organic solvents. With an alcoholic solution of picric acid it readily gives a *picrate* which crystallises from dilute alcohol in prisms, m.p. 120°. (Found: N, 12·39. $C_{18}H_{20}O_9N_4$ requires N, 12·8 per cent).

2:5-Dimethyl-6-ethylpyridine-3-carboxylic acid.—The above ethyl ester (5·5 g.) was heated under reflux with potassium hydroxide solution (15%, 25 c. c.) for more than one hour, and the solution filtered. The clear filtrate was made acid to Congo paper

with hydrochloric acid and the resulting solution was evaporated to dryness on a water-bath. The residue was extracted with absolute alcohol. The alcoholic solution (after charcoal treatment) was concentrated, cooled and diluted with ether, when the carboxylic acid separated out. This was crystallised from a mixture of alcohol and ether (1:1) and obtained in clusters of needles, m.p. 193-94° (decomp.). (Found: N, 7·54. $C_{10}H_{13}O_2N$ requires N, 7·82 per cent).

2:5-*Dimethyl*-6-*ethylpyridine*.—The above pyridine-β-carboxylic acid (1 part) was intimately mixed with finely powdered soda lime (about 3 parts) and the mixture was carefully heated under reduced pressure, when an oil was obtained. This was extracted with ether, the ethereal solution dried over anhydous sodium sulphate and the ether removed and the liquid distilled as a colourless liquid at 181-82°/756 mm. (Found: N, 10·28. $C_9H_{13}N$ requires N, 10·37 per cent). It possesses a characteristic smell and gradually darkens in colour. With an alcoholic solution of picric acid it gave a *picrate* which crystallised from alcohol (50%) in prismatic yellow needles, m. p. 127°. (Found: N, 15·26. $C_{15}H_{16}O_7N_4$ requires N, 15·38 per cent).

2:5-*Dimethyl*-6-*phenylpyridine*.—2 : 5-Dimethyl-6-phenylpyridine-3-carboxylic acid (1 part) obtained from the condensation of ethyl β-aminocrotonate with hydroxymethylene ethylphenylketone (*cf.* Basu, *loc. cit.*), was intimately mixed with powdered soda lime (3 parts) and the mixture was heated under reduced pressure as in the previous case. The oil obtained was extracted with ether and finally distilled at 285-87°/758 mm. The *picrate* was obtained as fine needles from alcohol, m. p. 180°. (Found: N, 13 66. $C_{19}H_{16}O_7N_4$ requires N, 13·59 per cent). The pyridine derivative is thus found to be identical with that previously obtained by Scholtz (*Ber.*, 1899, **32**, 1937).

2-*Methyl*-6-p-*tolylpyridine*.—2-Methyl-6-*p*-tolyl-pyridine-3-carboxylic acid (Basu, *loc. cit.*) was distilled with soda lime as in the previous cases and the oil obtained was distilled in *vacuo* at 291-92°/759 mm. as a colourless refracting liquid ; refractive index is 1·5970 at 37·5°. The *picrate* crystallised from alcohol in long prismatic needles, m. p. 146°. (Found: N, 13·34. $C_{19}H_{16}O_7N_4$ requires N, 13·59 per cent).

2:5:6-*Trimethylpyridine*, obtained by the distillation of 2:5:6-trimethylpyridine-3-carboxylic acid (Basu, *loc. cit.*) with lime, distilled at 176-78°/759 mm. Echert and Lorica ((*Monatsch.*, 1917,

38, 228) have isolated a similar pyridine base from coal tar and have recorded its boiling point as 173-74°/734 mm. and the m. p. of its picrate as 143-44°. The picrate of this product also melted at 144°. (Found: N, 16·10. $C_{14}H_{14}O_7N_4$ requires N, 16·0 per cent).

In conclusion we wish to express our sincere thanks to Professor Dr. H. K. Sen, for placing the resources of his laboratory at our disposal.

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The Coagulation of Ferrocyanide Sols containing Varying Amounts of Potassium Ferrocyanide.

BY NIRMALAPADA CHATTERJEE.

The part played by the adsorption of constituent ions in determining the electrical charge of inorganic colloids is fairly understood. The relationship observed by Lottermoser (*Z. physikal. Chem.*, 1908, **62**, 372) between the excess of the constituent ions present during the precipitation of similar halides and the sign of their charge find a simple explanation from the theoretical considerations of Mukherjee (*Trans. Faraday Soc.*, 1921, **16**, 103) who pointed out the importance of the lattice forces in determining the nature of the primarily adsorbed layer on the surface. The electro-osmotic observations of Mukherjee and co-workers (*J. Indian Chem. Soc.*, 1924 **31**, 178; 1926, **3**, 335, 371; 1927, **4**, 459) support the theoretical considerations. The relative adsorbabilities of such ions have been discussed by them with reference to barium sulphate, lead chromate and silver halides. It has been found that associated with the primarily adsorbed layer there is often present a secondary adsorption of hydrogen and hydroxyl ions which lead respectively to the liberation of alkali and acid from the double decomposition of the reacting neutral salts. With increasing concentration of adsorbable ions having the same sign of charge as the surface, frequently the electrical charge increases to a maximum and then diminishes. In conformity to this, the stability of the colloidal solution under such conditions as measured by the coagulating concentrations of an electrolyte has also often been found to pass through a maximum. The stability of a sol and

the cataphoretic velocity of its particles are, however, not directly related (*cf.* Mukherjee and co-workers, *J. Indian Chem. Soc.*, 1927, **4**, 493).

Neidle (*J. Amer. Chem. Soc.*, 1917, **39**, 2334) as also Sen (*J. Phys. Chem.*, 1925, **29**, 517) observed in the case of ferric hydroxide sol that in presence of an increasing concentration of hydrochloric acid, the stability towards potassium sulphate passes through a maximum. The primary adsorption of hydrogen ions on ferric hydroxide sol is quite strong but at high concentrations of hydrochloric acid, the electrical adsorption of chlorine ions may predominate. Sen (*loc. cit.*) and Weiser (*J. Phys. Chem.*, 1926, **30**, 20) studied the stabilising effect of the constituent ions, *e.g*, ferrocyanide ion on Prussian blue and copper ferrocyanide sol. With the progressive addition of potassium ferrocyanide, the stability towards potassium sulphate or chloride shows a similar maximum.

In the calculation of the coagulating value of an ion when mixtures of electrolytes are used, very often the total amount of the coagulating ions present in the system is not considered. From the results obtained by Sen (*loc. cit.*) and Weiser (*loc. cit.*) on the coagulating effect of potassium chloride on copper ferrocyanide sol, containing increasing amounts of potassium ferrocyanide it would appear that if the total concentration of potassium ions be taken into consideration, the coagulating value does not reach a maximum but increases continually. It was, therefore, thought desirable to test their point.

Dilution of a sol is known to affect the coagulating concentration of an electrolyte in several ways. It decreases the concentration of the particles and therefore the colloid-liquid interface decreases and also the distance between the particles increases. Mukherjee and Sen (*J. Chem. Soc.*, 1919, **115**, 461), as also Kruyt and Spek (*Kolloid Z.*, 1919, **25**, 1), pointed out that the decrease of the colloid-liquid interface increased the adsorption of an electrolyte per unit area of the surface and this would sensitise the sol. This effect would be negligible when monovalent precipitating ions are considered because the concentration of the electrolyte is high. On the other hand, the increased distance stabilises the sol by lessening the collisions between particles. The resultant effect of the two will decide whether the sol is stabilised or sensitised on dilution. When a sol containing an appreciable amount of the stabilising electrolyte is diluted, the concentration of the electrolyte diminishes but even

with the same colloidal substance both a sensitisation and a stabilisation has been observed. Weiser and Nicholas (*J. Phys. Chem.*, **25**, 742) and Ghosh and Dhar (*ibid.*, 1925, **29**, 159), determined the coagulating concentration of potassium chloride on different dilutions of Prussian blue sol. Weiser and Nicholas worked with a sol which contained considerable amount of potassium ferrocyanide and found that the sol became unstable on dilution. The sol used by Ghosh and Dhar was almost free from potassium ferrocyanide and a stabilisation was observed. In order to verify whether Weiser and Nicholas's contradictory observations were due to the presence of potassium ferrocyanide, Ghosh and Dhar (*J. Phys. Chem.*, 1927, **31**, 187) added to the sol considerable amount of the salt but they did not find any sensitisation.

In a previous paper (Chatterjee, *Kolloid Z.*, 1930, **52**, 214) the following results were obtained. (*a*) For uranium ferrocyanide sol containing additions of potassium ferrocyanide in concentrations proportionate to the dilution, the total amount of potassium ions necessary for coagulation with potassium chloride decreases with the dilution. (*b*) If the strength of free potassium ferrocyanide (0·005*N*) was kept constant for all the dilutions, the coagulating concentration decreased on dilution of the sol but the difference observed under (*a*) markedly diminishes and with thorium chloride, instead of a decrease, an increase in the coagulating concentration occurred. (*c*) When a fixed amount of a strong solution of potassium ferrocyanide was added to the same volume of all the dilutions, coagulation with potassium chloride shows stabilisation on dilution.

In the present work the same amount of potassium ferrocyanide was added to the dilutions of a number of ferrocyanide sols. The amount of the salt was gradually increased and the concentration of potassium chloride necessary to coagulate the sols were determined. The total concentration of cations is taken as a measure of the stability of the sol. The cations *being* the same in both the electrolytes, the antagonistic effect is absent. The coagulating concentrations of different electrolytes for the concentrated and dilute sols in absence of the added potassium ferrocyanide, were also determined.

By the usual method of preparation of ferrocyanide sols, the intermicellary liquid contains some amount of potassium ferrocyanide. Sols used in the present work were at first precipitated from an excess of the metallic salts and then the precipitate was centrifuged. The supernatant liquid was thrown away and fresh water was added

and the sol was centrifuged again. The process was repeated till peptisation occurred. The concentration of free electrolytes in the intermicellary liquid was thus considerably reduced.

The cataphoretic velocity was measured for the concentrated and the diluted sol of copper ferrocyanide containing the same amounts of potassium ferrocyanide solution. The p_H values of the ultrafiltrate of the above mixtures were also determined colorimetrically. Specific conductivities of the sols were also measured.

Preparation of sols.—A slight excess of an approximately normal solution of the chloride of the metal was mixed with a solution of potassium ferrocyanide of equivalent strength. In the case of uranyl ferrocyanide, the nitrate was used. The precipitates were washed and centrifuged; the supernatant liquid was discarded and the process repeated. The p_H value and specific conductivity of the supernatant liquids were determined. The ions present were also tested. After several washings in this way, the substance was peptised. The sols of Prussian blue, uranyl ferrocyanide and aluminium ferrocyanide had an acid while copper, zinc and cadmium ferrocyanide had an alkaline reaction.

The coagulating concentrations were determined in the previous paper (Chatterjee, *loc. cit.*) in the manner described by Mukherjee and Ghosh (*J. Indian Chem. Soc.*, 1924, **1**, 213). The coagulating concentration was determined in the present case differently. After adding the coagulating electrolyte to both dilutions of the sol, the sols were centrifuged for 8 minutes. The minimum concentration necessary for producing a clear supernatant liquid was taken as the equicoagulating concentration of an electrolyte.

In the following series, the coagulating concentrations of electrolytes for the sols and their dilution are given. Column (I) indicates the coagulating concentrations of electrolytes expressed in milliequivalents per litre. Column (II) indicates the activity of the coagulating concentrations of cations, calculated for the very dilute solutions, multiplied by 1000. For uniunivalent electrolytes, the simplified equation of Debye and Hückel has been used (Brönsted, *Trans. Faraday Soc.*, 1927, **33**, 416).

$$\log \gamma = \frac{-0{\cdot}5\sqrt{\mu}}{1+A\sqrt{\mu}}$$

Where γ denotes the activity coefficient of the ion; μ, the ionic strength of the electrolyte; A, a const. $=1{\cdot}65$ from Scatchard's data.

For electrolytes having ions of higher valency where $\sqrt{\mu}$ is less than 0·1, the following equation has been used:

Log $\gamma = 0{\cdot}5\ Z^2\sqrt{\mu}$, where Z is the valency of the ion.

The activity coefficients are only approximate specially at high concentrations. The activity coefficients, therefore, at high concentrations are not given in the tables.

Coagulating Concentration of Different Electrolytes on Ferrocyanide Sols and their Dilutions when no Potassium Ferrocyanide is Added.

TABLE I.

Uranium ferrocyanide sol.

	KNO_3		$AlCl_3$		$ThCl_4$		$K_3Fe(CN)_6$
Sol.	I	II	I	II	I	II	I
A	9	8·08	0·14	0·104	0·052	0·035	150
A/2	15	13·36	0·101	0·078	– 0·04	0·028	240
A/4	+20	17·58	−0·083	0·066			+306

TABLE II.

Prussian blue sol.

	$K_4Fe(CN)_6$	KCl		$AgNO_3$		$BaCl_2$		$AlCl_3$		$ThCl_4$	
Sol	I	I	II	I	II	I	II	I	II	I	II
A	280	10	9·08	0·375	?368	1·5	1·01	0·08	0·064	0·014	0·012
A/2	+300	+17·5	15·48	−0·300	0·294	+2	+1·41	−0 066	0·054	−0·0099	0·0083

The preceding tables show the usual behaviour on dilution (Mukherjee and Sen *loc. cit.*) namely the dilute sol requires higher concentration when the coagulating ion is univalent and a smaller one when these ions are polyvalent. Barium resembles a univalent ion in this respect. Silver ions resemble on the other hand the polyvalent ions in agreement with previous observation and with its known greater absorbability. The two factors—the stabilising effect produced by the diminution in the number of collisions, and the sensitising effect of the greater adsorption per unit surface of the more dilute sol (which would be more prominent for ions having a low

+ indicates a stabilisation on dilution,—a sensitisation and 0, neither stabilisation nor sensitisation.

coagulating concentration), are sufficient to account for the preceding observations. The coagulating concentration of potassium ferrocyanide is much larger than those of the nitrate or chloride in agreement with the expected greater adsorption of the constituent ferrocyanide ion. Table III shows that this is true of the other ferrocyanide sols. The differences in the coagulating concentration of potassium chloride for the two dilutions may be very small. For copper ferrocyanide, the two dilutions are coagulated at the same concentration. The addition of potassium ferrocyanide in small concentrations systematically increases the coagulating concentration of potassium ions. The dilute sol should therefore be less stable as the concentration of the free ferrocyanide would diminish on dilution. The stabilising effect of the greater distance between the particles on dilution, therefore, appears to be the predominating factor.

TABLE III.

	$Cu_2Fe(CN)_6$ Sol			$Zn_2Fe(CN)_6$ Sol		$Cd_2Fe(CN)_6$ Sol			$Al_4[Fe(CN)_6]_3$ Sol		
	KCl		$K_4Fe(CN)_6$.	KCl		KCl		$K_4Fe(CN)_6$.	KCl		$K_4Fe(CN)_6$.
Sol	I	II		I	II	I	II		I	II	II
A	19·2	16·9	400	2·6	2·45	5	4·62	848	5	4·62	250
A/2	19·2	16·9	+440	+2·9	2·73	+7·5	6·8	+900	+7·5	6·8	+300

In the previous paper (Chatterjee, *loc. cit.*) a sensitisation on dilution was observed against potassium chloride and nitrate in the case of uranium ferrocyanide sol which contained an appreciable amount of potassium ferrocyanide. As will be shown later the amount of the stabilising electrolyte, possibly also the number and *size* of the particles, influence the behaviour of the sol on dilution. Apart from the differences in these respects, the uranium ferrocyanide sol used in the earlier case contained some free potassium nitrate. Potassium nitrate was, therefore, added in amounts proportional to the dilution to the sol used in this work. The results are given in Table IV.

TABLE IV.

Sol.	KNO_3 added.	Coagulating conc. of electrolytes in m. equiv./litre.		
		KNO_3.	$AlCl_3$.	$ThCl_4$.
A	2 m. equiv./litre.	6·5	0·072	0·021
A/2	1	+12·5	−0·063	+0·023

With proportionate decrease of the amount of potassium nitrate added to the sols A and A/2, a stabilisation against thorium chloride, as observed previously, is again observed. The degree of sensitisation as measured by the percentage change in the coagulating concentration also diminishes for the other electrolytes. The coagulating concentrations measured by the method used in the present and that used in the earlier work show the same manner of variations with dilution.

The coagulating concentrations of potassium chloride were determined for two dilutions of each sol both containing the same amounts of potassium ferrocyanide. The amount of free potassium ferrocyanide in the sol is negligible in comparison with the amount added.

Columns (I) and (II) give as before the coagulating concentrations and activities respectively of the total number of cations of the added electrolytes.

TABLE V.

Conc. of $K_4Fe(CN)_6$ added are given in m. equiv. per litre.

Uranium ferrocyanide sol.

$K_4Fe(CN)_6$ added to sol.											
	0·05		0·2	2·0	4·0	25	50	100	250	750	1000
Sol.	I	II	I	I	I	I	I	I	I	I	I
A	21	18·5	157·2	352		810	920	1000	1210	1535	1700
A/2	+52	43·2	+175·2	352	+441	−725					−1525

Prussian blue sol.

$K_4Fe(CN)_6$ added to sol.						
	0·025	0·05	0·25	0·5	25	50
Sol.	I	I	I	I	I	I
A		70		357·5	207	2·4
A/2	87·5	+105	367·2	−350·5	−200	

Copper ferrocyanide sol.

$K_4Fe(CN)_6$ added.			
	0·10		100
Sol.	I	II	I
A	28	24·2	250
A/2	+29·4	25·3	−235

Zinc ferrocyanide sol.

$K_4Fe(CN)_6$ added.				
	0·10		50	200
Sol.	I	II	I	I
A	3·5	3·36	330	1075
A/2	+4·37	4·14	+347	+1110

Cadmium ferrocyanide sol.

$K_4Fe(CN)_6$ added.			
	0·10		200
Sol.	I	II	I
A	22·5	20·6	500
A/2	+30	25·8	+510

Aluminium ferrocyanide sol.

$K_4Fe(CN)_6$ added in m. equiv./litre.			
400	0·10		50
	I	II	I
Sol.	I	II	I
A	500	15	13·4	175
A/2	−490	+20	17·7	−150

FIG. 1.
Uranium Ferrocyanide sol.

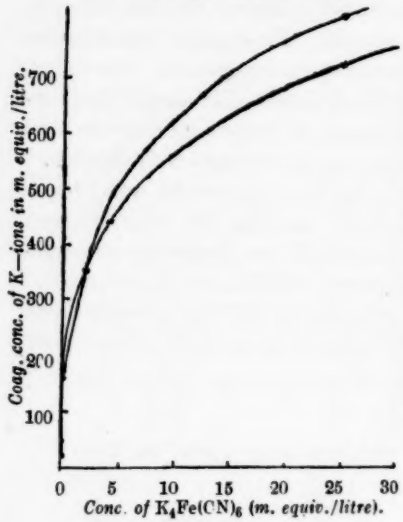


FIG. 2.
Prussian blue sol.

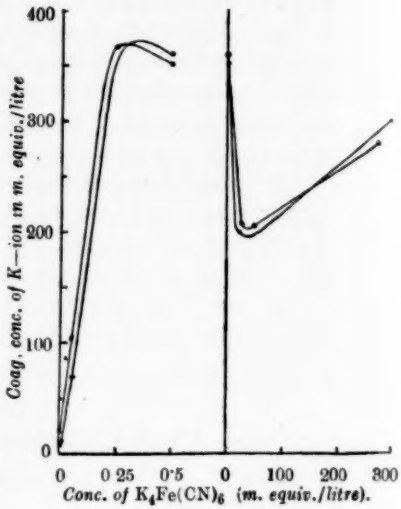


FIG. 3.
Copper ferrocyanide sol.

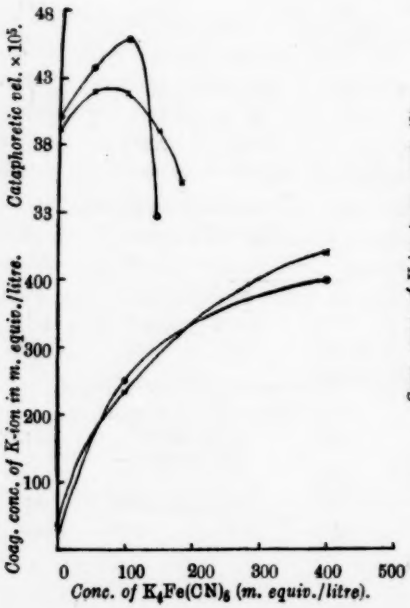
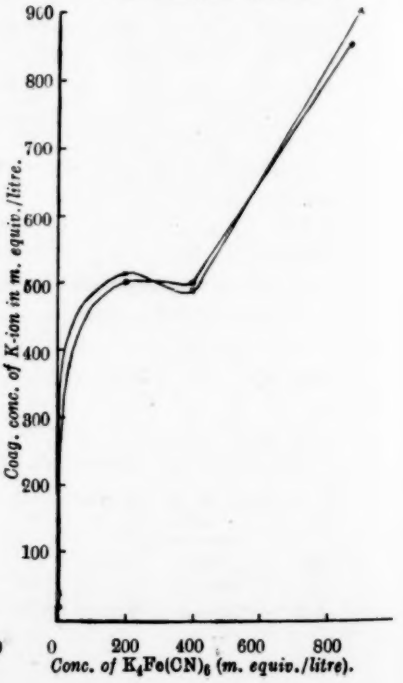


FIG. 4.
Cadmium ferrocyanide sol.



The curves in Fig. 1-5 show that in general the coagulating concentration increases with the concentration of the ferrocyanide so long as the latter is not large. At the higher concentration, the course of the curves becomes more complicated. The diluted sol is more stable, *i.e.*, it requires a higher coagulating concentration when the concentration of the ferrocyanide is low. In some cases at high concentrations it becomes less stable. The curves for the diluted sols have broadly speaking the same form as for the concentrated ones and the two curves appear to differ mainly in that one has been slightly displaced with respect to the other. The result is that if one of the curves shows a maximum, the two curves meet at same point, *e.g.*, at a concentration of 0·5 milliequivalents per litre of potassium ferrocyanide in the case of Prussian blue sol, and the stabilisation on dilution which is observed in the earlier part of the curve changes to a sensitisation on the other side of the curve. Where there is a minimum in addition to the maximum, the curves again intersect and the order is again reversed. A closer examination of the curves will show that the two curves are not parallel and the percentage change in the coagulating concentrations for every two concentrations of the ferrocyanide are different. The slopes of the curves inspite of the insufficient number of points convey the impression that the two sols while showing in the main a similarity in this behaviour also have minor differences.

The Prussian blue sol is acidic and the cadmium ferrocyanide sol is alkaline but they resemble each other in their behaviour. In the case of uranium, copper, aluminium and zinc ferrocyanide the coagulating value continually increases. Prussian blue and cadmium ferrocyanide both show a maximum followed by a minimum. The uranium and zinc ferrocyanide sols could not be coagulated with a saturated solution of potassium ferrocyanide. The diluted zinc ferrocyanide sol is more stable for the two concentrations of potassium ferrocyanide but the diluted uranium ferrocyanide sol shows a change from stabilisation to sensitisation similar to what has been observed with the others at high ferrocyanide concentration. The main interest of the preceding observation lies in that they show that the relationships are more complicated than those previously recorded. These observations help us to understand the different results observed by previous authors. Thus Ghosh and Dhar (*loc, cit.*) found in the case of Prussian blue sol a stabilisation with potassium chloride whereas a sensitisation was reported by Weiser and Nicholas (*loc. cit.*). The sol

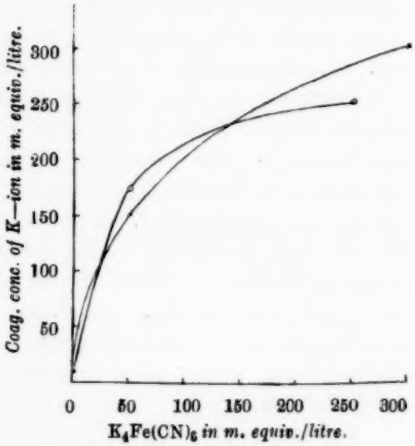
prepared by Ghosh and Dhar was free from potassium ferrocyanide while the preparation of Weiser and Nicholas contained some free potassium ferrocyanide. Ghosh and Dhar (*J. Phys. Chem.*, 1927, **31**, 187), therefore, added potassium ferrocyanide to the sol proportionate to the dilution and coagulated it with potassium chloride. But instead of a sensitisation they got a stabilisation as shown in the following table.

TABLE VI.

Sol.	$K_4Fe(CN)_6$ adddd in m. equiv. per litre.	The coag. conc. of KCl in m. equiv. per litre.
A	25	65·0
A/2	12·5	77·5
A/5	5	87·5

FIG. 5.

Aluminium ferrocyanide sol.



The concentration of potassium ferrocyanide used by Ghosh and Dhar (*loc. cit.*) was 25 to 5 m. equiv. per litre. It will be seen from Fig. 2 that the maximum for this sol lies between 0·05 and 0·5 m. equiv. per litre. In this region a sensitisation will be observed for the same sol if the concentration of the free ferrocyanide decreases. On the other hand, if the concentration of the free potassium ferrocyanide is above 0·5 m. equiv. per litre, then a stabilisation will take place if the ferrocyanide concentration decreases on dilution. In comparing the coagulating concentration of a diluted sol with the undiluted sol, the stabilising effect of the diminution in the concentration of the particles and the sensitisation due to a smaller interface are additional factors. The last factor has a small effect compared to the stabilisation resulting from the dilution of the ferrocyanide solution. The stabilisation observed by Ghosh and Dhar is thus to be ascribed to the high concentration of the ferrocyanide they used. It appears that the potassium ferrocyanide present in the sol of Weiser and

Nicholas contained potassium ferrocyanide between 0·5 and 0·05 m. equiv., *i.e.*, on the first ascending portion of the curve.

The comparison of the effect of dilution for the same concentration of the added potassium ferrocyanide has the advantage that one of the factors influencing the behaviour of the sol is maintained fairly constant. As has been shown above, the concentration of the stabilising ion affects the coagulating concentration of potassium ions considerably and in a complicated manner. If the amount of the ferrocyanide adsorbed by the particles is negligible compared to the total amount present, then its equilibrium concentration will be the same for both sols. If the amount adsorbed is not negligible, then also such a comparison has the advantage that the difference in the concentration of the stabilising ions for the two sols will be much smaller than what it is in the usual investigations on the effect of dilutions. The differences in the equilibrium concentration for the two sols should also decrease for as the concentration of the ferrocyanide increases, the amount adsorbed will be increasingly a smaller fraction of the total amount present. Under such circumstances the stabilising effect of the smaller concentration of the particles of the diluted sol should preponderate.

The change from stabilisation to sensitisation on dilution observed in several cases cannot be explained by the above considerations. They cannot also account for the minimum observed with the same sol. In the above discussion it has been assumed that the composition and distribution of ions in the double layer which determine the electrical condition of the particles of both sols is determined simply by the equilibrium concentration of the ferrocyanide ions. Recent measurements of cataphoretic speeds give indications of changes of a more complicated nature with dilution of a sol (Mukherjee, Raichaudhuri and Biswas, *J. Indian Chem. Soc.*, 1931, **8**, 373; S. N. Mukherjee, *Kolloid Z.*, 1930, **52**, 63). Solutions of potassium ferrocyanide are also slightly hydrolysed and the relative proportion of potassium to hydrogen ions associated with the adsorbed ferrocyanide ions may be different from that in the solution. Comparatively small changes in the interface can considerably affect the equilibrium distribution of free ions in the intermicellary solution even when the free electrolyte is present in high concentration. Thus variation of small amounts of silica in contact with normal potassium chloride solution alters perceptibly the hydrogen ion concentration of the supernatant liquid (Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**,

191). Exact information in these aspects will be materially helpful in understanding the above observations. One of the point that emerges from the above is that it should be ascertained whether the amounts adsorbed appreciably alter the total concentration of the ferrocyanide ions. For this purpose the specific conductivity of the copper ferrocyanide sols and their ultrafiltrates and the p_H of the latter were determined. The ultrafiltrate was obtained with freshly prepared well-washed collodion membranes. A small portion of the ultrafiltrate which comes out first was not collected. The ultrafiltrate collected was a small fraction of the sol in the ultrafilter, so that its composition is not altered to a large extent as a result of the ultrafiltration. The results are given below.

TABLE VII.

Copper ferrocyanide sol.

Concentrations of $K_4Fe(CN)_6$ are given in milliequivalents per litre and specific conductivity given in mhos $\times 10^4$. Temp. $= 28° + 1$.

Sol A

	Pure sol		Contains 2·5 m.e $K_4Fe(CN)_6$		Contains 100 m.e. $K_4Fe(CN)_6$	
	Sol.	Ultrafiltrate.	Sol.	Ultrafiltrate.	Sol.	Ultrafiltrate.
Sp. conducty.	0·3	0·1	2·4	1·9	95·2	94·6
p_H		6·67		7·57		8·35

Sol A/4

Sp. conducty.	0·1	0·048	3·5	3·3	99·3	98·8
p_H		6·59		7·53		8·33

$K_4Fe(CN)_6$ solution.

	Water.	2·5 m.e. $K_4Fe(CN)_6$	100 m.e. $K_4Fe(CN)_6$
Sp. conducty.	0·017	4·2	100
p_H	6·55	7·37	7·88

The specific conductivities for the sols containing potassium ferrocyanide are less than that of a solution of the salt having the same concentration although the sol itself has appreciable conductivity. The dilute sol is more conducting than the concentrated sol. The percentage difference between the specific conductivities of the

sols and of corresponding concentrations of the salt decreases as the concentration of the latter increases. The adsorption of the electrolyte is thus perceptible even for decinormal potassium ferrocyanide and the equilibrium concentration of the ferrocyanide is higher for the dilute sol. For the sols containing decinormal potassium ferrocyanide, the equilibrium concentration differs only slightly being about 4% as indicated by the percentage difference in the conductivity. The specific conductivities of the ultrafiltrate lend additional support to these conclusions. On account of a possible effect of Donnan equilibrium the ultrafiltrate may not have the same composition as the intermicellary liquid but it supplies useful corroborative evidence and indications of the relative composition of the intermicellary liquid. The ultrafiltrate has a higher p_H than the potassium ferrocyanide solution which may be taken to indicate that part of the ferrocyanide removed by adsorption takes with it some hydrogen ions to the interface by electrical adsorption. The amount of hydrogen ions so removed is greater than that indicated by the change in the p_H as the salt would exert a buffer effect. The ratio of hydrogen to potassium ions associated with the adsorbed ferrocyanide ions is thus greater than in a solution of potassium ferrocyanide of the same strength. These results give a clear idea of the behaviour of the sol on dilution. The displacement of the curve for the dilute sol relative to the other implies that the equilibrium concentration of the ferrocyanide of the dilute sol is throughout higher than that of the concentrated sol. The dilute sol, therefore, requires a higher coagulating concentration for its coagulation, so long as an increase of the concentration of the ferrocyanide is associated with an increase in the coagulating concentration. In this region the stabilising effect of the diminution of the concentration of the colloidal particles is added to that of a greater adsorption of the ferrocyanide ions per unit area. The dilute sol should also reach the maximum earlier as it actually does in some cases. Just after the maximum has been reached the stabilising effect of a greater separation of particles persists but increasing concentrations of the ferrocyanide decreases the coagulating concentration, but that of the undiluted sol just near the maximum of the dilute sol continues to increase. Thereafter the coagulating concentration decreases for both but at different rates depending on the differences in the slopes of the respective curves. The resulting difference in the stability overweighs the difference produced by the smaller number of collisions of particles of the dilute

sol. It is more difficult to account for the second minimum observed in some cases and the persistence of the displacement at very high concentrations where one would expect that the equilibrium concentration will be the same for both sols. The diluted sol should require a higher coagulating concentration. But the coagulating concentration for the dilute uranium ferrocyanide sol is less although the sols contain normal potassium ferrocyanide. It is difficult to assume that at such high concentrations the amount adsorbed produces a material difference in the equilibrium concentration of the ferrocyanide. Moreover, it has been already mentioned that the diluted sol shows definite differences regarding the manner in which the coagulating concentration changes with the concentration of the ferrocyanide.

The relative electrical adsorption of hydrogen and ferrocyanide ions suggest a way out of the difficulty. It has been mentioned that the ultrafiltrates are more alkaline than corresponding solutions of the ferrocyanide. The ultrafiltrate of the concentrated sol has the same (perhaps slightly higher) p_H as the dilute sol though the latter contains more free ferrocyanide ions. Higher concentrations of the ferrocyanide have higher p_H and the relative adsorption of hydrogen ion should decrease as their concentration rapidly decreases. The electrical adsorption of potassium ions being comparatively weak, the density of the free negative charge may increase inspite of the increasing concentration of potassium ions. In other words slight changes in p_H can affect the charge considerably. Measurements of cataphoretic speeds would afford useful information.

The charge of the copper ferrocyanide sol in two dilutions in presence of different amounts of potassium ferrocyanide solution was measured by the boundary method (Mukherjee, *Proc. Roy. Soc.*, 1923, **103A**, 102).

TABLE VIII.

The cataphoretic speed is given in cm. per sec. per unit potential gradient $\times 10^5$. Temp. = 35°.

	$K_4Fe(CN)_6$ added in m. equiv./litre.				
	2·5	50	100	150	187
Sol 1 :1	40·78	43·91	46·43	33·1	
Sol 1 :7	39·07	42·02	42·19	39·36	35·65*

The cataphoretic velocity passes through a maximum for both sols and at low concentrations, the cataphoretic velocity of the dilute sol

* Coagulation commences during measurement.

is less than that of the other. The latter observation indicates that the higher equilibrium concentration of the ferrocyanide ions which should obtain for the dilute sol does not necessarily mean a greater cataphoretic velocity. At 150 milliequivalents of the ferrocyanide ion, the cataphoretic velocity of the dilute sol is greater. The measurements of cataphoretic speeds for the electrolyte mixtures corresponding to the coagulating systems are also necessary as they may bring out quite different relationships from the above. More extensive measurements are apparently necessary.

The work was carried out in the physical chemistry laboratory, Calcutta University, as a University research scholar from 1930 to 1932 but could not be continued as the writer got an employment.

The author thanks the University of Calcutta for the award of a research scholarship and Prof. J. N. Mukherjee for his advice and facilities for this work.

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Preparation of Resorcinol Monomethyl Ether (A Correction).

By B. B. Dey.

My attention has been drawn to certain inaccuracies of a grave character in the details of the method of preparing this substance which appeared in this Journal (1934, **11**, 743; 1935, **12**, 141). Resorcinol monomethyl ether is practically non-volatile in steam. The correct method is described below.

A solution of pure resorcinol (11 g.) in 10 % caustic soda (40 c.c.) was warmed to 60°-70° and treated with good shaking with pure acid-free dimethyl sulphate (12-13 g.) added in small quantities at a time. The mixture was finally heated on the boiling water-bath for ½ hour. It was extracted, on cooling, with ether (30 c.c., 25 c.c. and 20 c.c.), the ethereal solution extracted with 10%

caustic soda (80 c c., 20 c.c.), the alkaline solution acidified in the cold (ice) with HCl (1:1) and the whole then extracted thrice with ether (50, 25 and 20 c.c.). The ethereal solution was dried over calcium chloride, the ether removed on the water-bath and the residue distilled from a small flask (50 c.c.). The fraction passing between 240°—248° was collected. The amount of the ether, a pale yellow thick oil, obtained in two different experiments, weighed 7·3 g. and 7·4 g. respectively.

The results obtained on carrying out the operation according to the wrong instructions given might also prove to be of interest: On distilling in steam for 2 hours a pale yellow oil (about 2 c.c.) passed over; on treating the distillate in the manner described, 1·5 c.c. of a colourless oil, b p. 210°-212°, was isolated and identified with resorcinol dimethyl ether, while hardly a drop of a dark coloured oil soluble in alkali, which might be the monomethyl ether, was obtained. The residual liquid in the steam distillation flask was made alkaline and extracted with ether which removed only a trace of the dimethyl ether. The solution was then acidified and the monomethyl ether which separated as a dark oil was extracted with ether, dried and distilled, yield 6 g. of product (b. p. 240°-250°).

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As the work had been carried out some four years ago I had to consult the old files containing records of work carried out by students in my laboratory. I find that the wrong method had been copied for a thesis by one of my students without regard to a marginal note in my own handwriting in which the correct method had been described. Messrs V. Mahadevan and G. Srinivasan have now carefully repeated the preparation by the correct method under my supervision.

On the Colour Reaction of Certain Nitro Compounds.

By Prafulla Kumar Bose and Sundar Ram

m-Dinitrobenzene gives an unstable violet colour with laevulose in alkaline solution. This observation was made by Chavassieu and Morel (*Compt. rend.*, 1906, **143**, 966). Quite recently Truhaut (*J. Pharm. chim.*, 1933, **125**, 339) has observed that the same nitro compound gives a stable and characteristic violet colour with uric acid in alkaline medium. This observation of Truhaut has been criticised by Bose (*Current Science*, 1934, **2**, 427) who has proved that absolutely *pure* *m*-dinitrobenzene does not give any colour reaction of the above type whereas *o*-dinitrobenzene even in traces does so. The colour reactions observed by Truhaut and by Chavassieu and Morel are due to traces of *o*-dinitrobenzene present as impurity in *m*-dinitrobenzene. Bose has further demonstrated that *o*-dinitrobenzene gives the same characteristic violet colour with aldoses and ketoses (*Z. anal. Chem.*, 1932, **87**, 110) as also with polyhydroxybenzenes having at least two hydroxy-groups in the *para*- or *ortho*-position to one another (*J. Indian Chem. Soc., Sir P. C. Rây Volume*, 1933, p. 65).

Quite recently Péronnet and Truhaut (*Bull. Soc. chim.*, 1933, **53-54**, 1465) have further described a method for the determination of benzene vapour in air based on the conversion of benzene into *m*-dinitrobenzene by the action of a mixture of fuming nitric and concentrated sulphuric acids at a low temperature, and by measuring the intensity of colour developed by the '*m*-dinitrobenzene' in alcoholic and alkaline solution with the reducing sugar laevulose under certain experimental conditions. What happens in this case is that a certain amount of *o*-dinitrobenzene is formed as a bye-product during the nitration of benzene and this *ortho*-compound gives the colour reaction. The success of the method, therefore, would depend on two factors:

(*i*) The nitration must be carried out under definite experimental conditions, since variations of temperature, concentration of acids, etc., would result in a variation of the amount of *o*-dinitrobenzene formed.

(*ii*) A sufficient amount of impure *m*-dinitrobenzene (25-125 mg.) must be used for the colorimetry. A smaller amount would contain too little *ortho*-compound to give a stable colour.

In this connection it seemed desirable to study the behaviour of *ortho*-dinitro compounds in general towards alkaline reducing agents specially towards an alkaline solution of uric acid. The nitro compounds were taken in the form of 1-0·5% solution in absolute alcohol and 1-2 drops of this solution were added to 1 c.c. of a solution of uric acid (2·5 g. of acid dissolved in 100 c.c. of water containing 2·5 g. of potassium hydroxide) and the mixture heated on a boiling water-bath. In some cases a colouration was observed at room temperature which either deepened or changed on being further heated. The following table shows the results obtained.

TABLE I.

Substance.	Colour reaction	
	At 25°.	At 100°.
1 :2-Dinitrobenzene	Violet	Deep violet
4-Chloro-1 :2-dinitrobenzene	,,	Bluish violet
3 :4-Dichloro-1 :2-dinitrobenzene	...	Cherry-red
3 :5-Dichloro-1:2-dinitrobenzene	Violet	Bluish violet
3 :6-Dichloro-1 :2-dinitrobenzene	...	Yellow
4 :5-Dichloro-1 :2-dinitrobenzene	Violet	Indigo blue
3 :4 :5-Trichloro-1 :2-dinitrobenzene	Greenish yellow	Purplish brown
2 :3-Dinitrotoluene	...	Violet
3 :4-Dinitrotoluene	...	,,
2 :3-Dinitroanisole	...	,,
3 :4-Dinitroanisole	...	,,
2 :3-Dinitroaniline	Yellow	Yellow
2:3-Dinitroacetanilide	Pale green	Violet
3 :4-Dinitroaniline	...	,,
3 :4-Dinitroacetanilide	...	Reddish violet
6-Chloro-2 :3-dinitroaniline	Yellow	Violet
6-Chloro-2 :3-dinitroacetanilide	Straw yellow	Yellow
2 :5-Dichloro-3 :4-dinitroacetanilide	Greenish yellow	Greenish yellow
1 :2 :3-Trinitrobenzene	Violet brown	Violet-brown
4-Chloro-1 :2 :3-trinitrobenzene	Dirty violet	Dirty violet
5-Chloro-1 :2 :3-trinitrobenzene	,,	,,
1 :2 :4-Trinitrobenzene	Yellow brown	Yellow brown
6-Chloro-1 :2 :4-trinitrobenzene	Brown	Brown
1 :4-Dinitrobenzene	,,	,,
2 :3:4:6-Tetranitrophenol	Orange	Orange
3 :4-Dinitro-o-xylene	Cherry red	Cherry-red

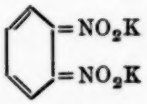
From the foregoing results certain conclusions can be drawn thus:

(*i*) Aromatic *o*-dinitro compounds in general develop with suitable reducing substances in alkaline medium colour varying from cherry red to indigo-blue.

(*ii*) Chlorine atoms or NH_2- groups in the proximity of the *ortho*-nitro groups hinder the development of any colour but yellow.

(*iii*) Compounds having nitro groups in the *para*-position to one another develop yellow to brown colour.

The development of colour in the above instances is to be attributed to the quinonoid salt of the type



and this has been definitely proved by Meisenheimer (*Ber.*, 1903, **36**, 4174) in the case of *o*-dinitrobenzene.

In conclusion, we wish to express our best thanks to Profs. A. F. Holleman and J. P. Wibaut for a gift of most of the compounds used in this investigation.

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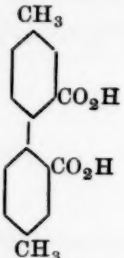
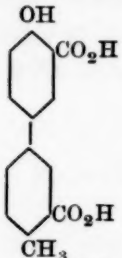
Studies in Diphenyl Series. Part IV. Action of Oxalyl Chloride on Diphenyl Derivatives.

By Nripendranath Chatterjee.

The action of oxalyl chloride on *pp'*-substituted diphenyl has been studied by Libermann and his co-workers (*Ber.*, 1911, **44**, 1453). They observed that *pp'*-ditolyl gave with oxalyl chloride 4 : 4'-dimethyl-2 : 7-phenanthrenequinone and 4 : 4'-dimethyldiphenic acid (I). However,



(I)

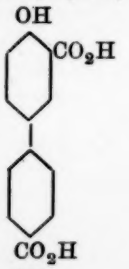


(II)

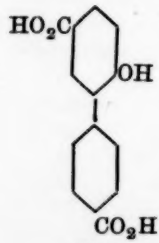
they observed the formation of only monocarboxylic acid in the case of *pp'*-dianisyl.

It has now been found that 4-methoxy-4'-methyldiphenyl (obtained by allowing a *p*-diazonium salt of toluene to react with phenol and afterwards methylating the hydroxydiphenyl obtained with dimethyl sulphate) condenses with oxalyl chloride in presence of aluminium chloride to give 4-methyl-4'-hydroxy-3 : 3'-dicarboxydiphenyl (II) as it gives the ferric chloride reaction for *o*-hydroxy acids and on oxidation 4-methyl-*iso*phthalic acid is obtained.

4-Methoxy and 2-methoxydiphenyl (*Ber.*, 1890, **23**, 2705) gave with oxalyl chloride 4-hydroxy-4' : 3-dicarboxydiph enyl (III) and 2-hydroxy-4' : 5-carboxydiphenyl (IV) respectively



(III)



(IV)

The constitution of these products has been proved by the ferric chloride reaction (III positive, IV negative) and by oxidation with alkaline permanganate, both giving terephthalic acid. The diphenyl acids were purified through their acetyl derivatives.

Experimental

4-Methoxy-4'-methyldiphenyl.—4-Hydroxy-4'-methyldiphenyl was treated with 15% NaOH solution when the sodium salt was precipitated. After adding an excess of dimethyl sulphate, it was heated on a water-bath for half an hour with frequent shaking. The product was extracted with ether and finally crystallised from ether, m. p. 112°. (Found: C, 84·7; H, 7·0. $C_{14}H_{14}O$ requires C, 84·8; H, 7·0 per cent).

4-Hydroxy-3:3'-dicarboxy-4'-methyldiphenyl.—A solution of 4-methoxy-4'-methyldiphenyl (5 g.) in carbon disulphide (50 c.c.) was treated with oxalyl chloride (13 g.) at 0° under stirring and then gradually with anhydrous aluminium chloride (5 g.). After $1\frac{1}{2}$ hours it was further treated with carbon disulphide (25 c.c.) and aluminium chloride (4 g.) and the stirring was continued for 6 hours and the dark green product was treated with sodium carbonate solution and distilled in steam. The residue was filtered off and the filtrate acidified. The precipitate was boiled with calcium carbonate and the resulting solution filtered and acidified. The crude acid precipitated was converted into the corresponding acetyl derivative by boiling with acetic anhydride in presence of a drop of pyridine, m. p. 204°. (Found: C, 64·5; H, 4·1; M. W., 313. $C_{17}H_{14}O_6$ requires C, 64·9; H. 4·4 per cent. M. W., 314). By deacetylation 4-hydroxy-3:3'-dicarboxy-4-methyldiphenyl was obtained, m. p. 280°. (Found: C, 65·9; H, 4·2. $C_{15}H_{12}O_5$ requires C, 66·1; H, 4·4 per cent).

Oxidation of 4-Hydroxy 3:3'-dicarboxy-4'-methyldiphenyl.—A solution of the substance (1 g.) in caustic potash (100 c. c., 1%) was treated gradually below 15° with $KMnO_4$ (500 c. c., 1%) until the colour persisted. MnO_2 was dissolved by treating with SO_2 and 4-methyl*iso*-phthalic acid (m. p. 320°) was precipitated by adding the calculated quantity of HCl (*d* 1·19). (Found: C, 59·8; H, 4·4. Calc. for $C_9H_8O_4$: requires C, 60·0; H, 4·4 per cent).

By a similar process described above, the following two compounds were also prepared:

4-Hydroxy-3:4'-dicarboxydiphenyl, m. p. 304°. (Found: C, 65·3; H, 3·6. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·8 per cent).

The *acetyl* derivative melts at 280°. (Found: C, 63·7; H, 3·8; M. W., 300. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0 per cent. M. W., 298). 4-Hydroxy-3:4′-dicarboxydiphenyl was oxidised as before and terephthalic acid identified as its methyl ester.

2-Hydroxy-5:4′-dicarboxydiphenyl melts above 300°. (Found: C, 64·8; H, 3·5. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·8 per cent).

The *acetyl* derivative melts above 300°. (Found: C, 63·6; H, 3·6; M. W. 299. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0 per cent. M. W., 300).

2-Hydroxy-5:4′-dicarboxydiphenyl was oxidised as before and terephthalic acid identified as its methyl ester.

In conclusion the author desires to express his grateful thanks to Prof. P. C. Mitter for much encouragement and advice during the course of this work.

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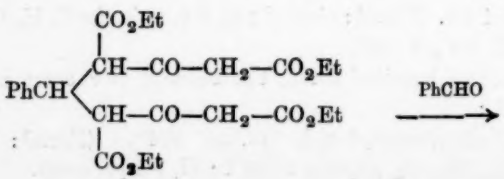
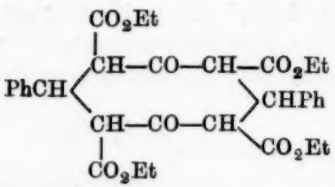
Extension of Michael's Reaction. Part V.

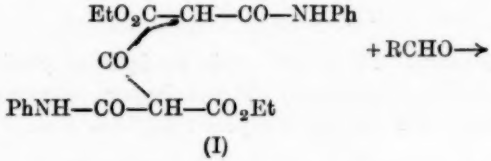
BY TEJENDRA NATH GHOSH.

In Part IV (*J. Indian Chem. Soc.*, 1934, **11**, 355) it has been shown that $\alpha\alpha'$-phenylcarbamylacetone dicarboxylate which contains two active hydrogen atoms in 1:3-position reacts readily with benzaldehyde to yield a compound which, in all probability, possesses a tricyclic structure. A very notable feature of this compound is its remarkable stability towards acid and alkali inspite of its complex molecular structure. In this connection mention should be made of an analogous observation of Knoevenagel (*Annalen*, 1895, **288**, 347) which shows that benzylidenebisacetone dicarboxylic ester, obtained by condensing acetone dicarboxylic ester with benzaldehyde, reacts with another molecule of the aldehyde to yield the following ring-compound

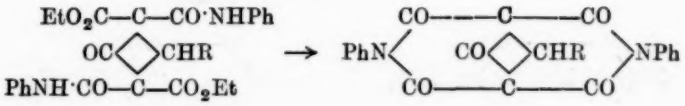




It has now been found that the first stage of the condensation of $\alpha\alpha'$-phenylcarbamylacetone dicarboxylate (I) with aldehydes involves the formation of the *cyclo*butane ring (II) which, under certain suitable conditions, yields the tricyclic ring (III) with the elimination of two molecules of alcohol.



(I)

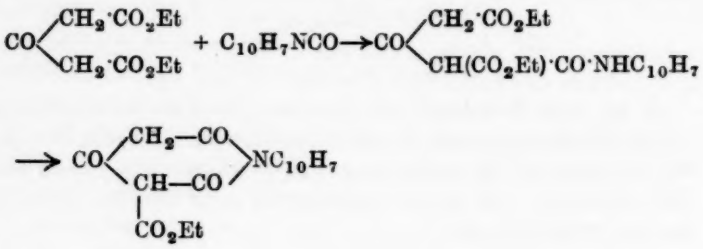


(II) (III)

The group R plays a very important part in the formation of the tricyclic ring (III) from the *cyclo*butane ring (II). The compound (III) is always obtained when the group R is C_6H_5, $C_6H_4NO_2$, $C_6H_4(OCH_3)$ or PhCH=CH. If, however, the ester (I) is condensed, under exactly similar conditions, with formaldehyde or acetaldehyde (R=H or CH_3), the *cyclo*butane ring (II) is obtained. It is, therefore, evident that the formation of the tricyclic ring is conditioned by the atomic volume of the group R. In other words, the greater the atomic volume of the group R, the more will be the tendency of the *cyclo*butane ring to pass into the tricyclic ring.

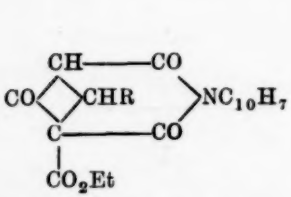
In order to ascertain the effect of two groups of high atomic volume (methyl and phenyl), the condensation of $\alpha\alpha'$-phenylcarbamylacetone dicarboxylate with acetophenone has been tried in presence of acetic anhydride. Two compounds have been isolated, one of which (m.p. 303-4° decomp.) is insoluble in alkali, the other (m.p. 224-25° decomp.) being soluble in alkali. Unfortunately, the yield of these two compounds is too poor to allow any further studies.

The sodium derivative of ethyl acetone dicarboxylate reacts with α-naphthyl *iso*cyanate to give a piperidine compound (IV) instead of the open-chain dinaphthylcarbamyl derivative analogous to compound (I).

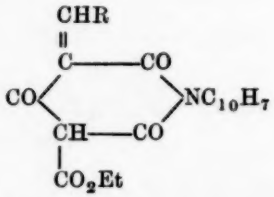


(IV)

The compound (IV) reacts with aldehyde to yield a compound which can be represented by either of the two following formulæ (V) and (V*a*). The original compound (IV) has been found to give a



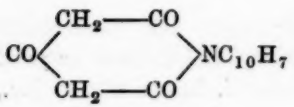
(V)



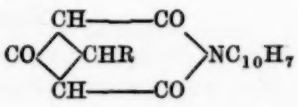
(V*a*)

monosodium derivative, whereas the aldehyde compound does not form any sodium salt. In view of the fact that a compound containing the system -CO-CH(CO_2Et)-CO- as in the formula (V*a*) should be acidic in nature, the formula (V*a*) is rejected in preference to the bridged formula (V) in which enolisation cannot take place according to Bredt's law (*cf.* Ghosh and Guha, *J. Indian Chem. Soc.*, 1934, **11**, 354).

The compound (IV) gets easily hydrolysed by alkali to yield the compound (VI). It was expected that the compound (VI), by reason of the presence of two active methylene groups, would react with two molecules of aldehyde; but it is, however, interesting to note that it reacts actually with one molecule of aldehyde to yield the bridged compound (VII), the constitution of which is confirmed by the fact that the aldehyde compound is insoluble in alkali.

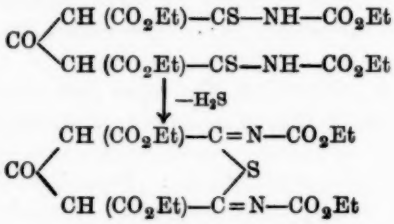


(VI)



(VII)

Ethyl acetone dicarboxylate reacts with carbethoxythiocarbimide to give a thiopyran compound (VIII) according to the following scheme. The compound is not endowed with any mercaptanic property and cannot be desulphurised by oxide of mercury confirming thereby the presence of the sulphur atom as a member of the ring.



VIII

In part IV (*loc. cit.*, p. 354) it has been shown that, under all conditions, only one molecule of phenylthiocarbimide reacts with ethyl acetone dicarboxylate to yield a thiopyran compound, whereas in the above reaction carbethoxythiocarbimide attacks both the methylene groups of ethyl acetone dicarboxylate. The greater reactivity of carbethoxythiocarbimide can be explained on the basis that the carbethoxy group, which has much smaller affinity demand than phenyl, endows the unsaturated group C=S in thiocarbimide with more residual affinity and hence, greater additive power (*cf.* Ingold and Weaver, *J. Chem. Soc.*, 1925, **127**, 378; Ghosh and Guha, *J. Indian Inst. Sci.*, 1933, **16A**, 105). It follows, therefore, that naphthyl *iso*cyanate, in which there are two fused benzene rings, should be less reactive than phenyl *iso*cyanate, which is actually the case as is evinced by a comparison of the compounds (I and IV).

The disodium derivative of 2:6-diketo-4:4-dimethyl*cyclo*hexane-3:5-dicarboxylate does not react with phenyl *iso*cyanate. It is significant to note that this fact is not singular but is observed amongst other homocyclic compounds, and that in all probability an important generalisation with regard to the inactivity of the sodium derivatives of homocyclic compounds in Michael's reaction is involved.

Experimental.

Ethyl aa'-phenylcarbamylacetone dicarboxylate (I) was prepared according to the method of Ghosh and Guha (*J. Indian Chem. Soc.*, 1934, **11**, 359).

Action of formaldehyde upon compound (I): *Formation of ethyl 2:4-diphenylcarbamido-cyclobutanone-2:4-dicarboxylate* (II, R=H).—To a boiling acetic acid solution of the compound (I), excess of formaldehyde was added. The solution was heated under reflux for about 30 minutes, when on cooling a brown solid was obtained which crystallised from acetic acid in brownish white rectangular plates, m. p. 248° (decomp.). (Found: C, 63·38; H, 5·69; N, 6·17. $C_{24}H_{24}O_7N_2$ requires C, 63·72; H, 5·31; N, 6·19 per cent). It is soluble in alkali and precipitated by acids.

The *semicarbazone* was obtained in the usual manner and was crystallised from dilute acetic acid in colourless rectangular plates, m.p. above 270°.

Action of acetaldehyde upon compound (I): *Formation of ethyl 2:4-dyphenylcarbamido-3-methylcyclobutanone-2:4-dicarboxylate* (II, R=CH_3).—The method of procedure was the same as in the case of the above compound. The reddish brown product was purified by precipitation by acid from its solution in alkali and was finally crystallised from a mixture of acetic acid and alcohol in brownish white rectangular plates, m p. 200-202° (decomp.). (Found: C, 64·01; H, 5·86. $C_{25}H_{26}O_7N_2$ requires C, 64·37; H, 5·58 per cent). It is soluble in alkali.

Action of salicylaldehyde methylether upon compound (I): *Formation of compound* [III, R=$C_6H_4(OCH_3)$].—The method of procedure was the same as in the case of the previous compounds. The product was crystallised from glacial acetic acid in fine yellow rectangular plates, m. p. 205-206°. (Found: C, 69·27; H, 4·28. $C_{27}H_{18}O_6N_2$ requires C, 69·54; H, 3·86 per cent). It is insoluble in alkali.

Action of cinnamic aldehyde upon compound (I): *Formation of compound* (III, R=PhCH:CH).—The method of precedure was the same as in the case of the previous compounds. The product was crystallised from a large quantity of glacial acetic acid in fine orange needles, m. p. 249-50° (decomp.). (Found: C, 73·06; H, 3·58. $C_{28}H_{18}O_5N_2$ requires C, 72·73; H, 3·89 per cent). It is insoluble in alkali and sparingly soluble in alcohol.

Action of acetophenone upon compound (I).—An acetic anhydride solution of the equimolecular proportions of the compound (I) and

acetophenone was heated under reflux for about 2 hours, when on cooling and standing for sufficiently long time, a very small quantity of yellow crystalline solid was obtained. A part of the product was soluble in alkali and was precipitated by acids and crystallised from acetic acid in brownish white rectangular plates, m.p. 224-25° (decomp.). The alkali-insoluble portion crystallised from a large quantity of glacial acetic acid in light yellow rectangular plates, m.p. 303-304° (decomp.). The yield of both the compounds was too poor to allow any further studies. From the mother-liquor, however, only a tarry product was obtained by evaporation or dilution with water.

1-Naphthyl-3-carbethoxy-2 : 4 : 6-triketopiperidine (IV).—Sodium (2·3 g.) was gradually added to a solution of ethyl acetone dicarboxylate (10·2 g.) in absolute ether (200 c.c.). After the evolution of hydrogen had ceased, α-naphthyl *iso*cyanate (8·5 g.) was added to the solution when the reaction commenced immediately. The precipitate was filtered overnight, dissolved in water and acidified with dilute hydrochloric acid when a solid separated which crystallised from glacial acetic acid in colourless rectangular plates, m. p. 191-92° (decomp.), yield 14 g. [Found: C, 66·22; H, 4·98; N, 4·16; M. W. (by titration), 325. $C_{18}H_{15}O_5N$ requires C, 66·46; H, 4·61; N, 4·31 per cent. M.W., 325]. It has been found by titration with standard caustic soda solution that it forms monosodium salt.

The same compound (IV) was obtained when α-naphthyl *iso*cyanate (2 mols.) was allowed to react with ethyl acetone dicarboxylate (1 mol.).

1-Naphthyl-3-carbethoxy-3 : 5-cinnamylidene-2 : 4 : 6-triketopiperidine (V, R=PhCH:CH).—An acetic acid solution of equimolecular proportions of the compound (IV) and cinnamic aldehyde was heated under reflux for about an hour. On cooling, a crystalline precipitate soon separated which crystallised from acetic acid in beautiful orange plates, m. p. 236-37° (decomp.). (Found: C, 73·51; H, 5·17. $C_{27}H_{21}O_5N$ requires C, 73·80; H, 4·78 per cent). It is sparingly soluble in alcohol and insoluble in alkali.

1-Naphthyl-3-carbethoxy-3 : 5-o-nitrobenzylidene-2 : 4 : 6-triketopiperidine (V, R=*o*-nitrophenyl).—The method of procedure was the same as in the case of the above compound. The product crystallised from glacial acetic acid in reddish brown rectangular plates, m. p. above 300°. (Found: N, 6·32. $C_{25}H_{18}O_7N_2$ requires N, 6·11 per cent). It is insoluble in alkali.

Hydrolysis of compound (IV): *Fomation of 1-naphthyl-2 : 4 : 6-triketopiperidine* (VI).—The above compound (IV) (10 g.) was heated

under reflux with alcoholic potash (15%) for about 8 hours and the alcohol was then distilled under reduced pressure. The solid was treated with water and acidified with dilute hydrochloric acid, when there was evolution of carbon dioxide. The solid thus obtained crystallised from glacial acetic acid in colourless rectangular plates, m.p. 249-50° (decomp.), yield 5·5 g. It is insoluble in aqueous bicarbonate solution but readily soluble in alkali. (Found: C, 70·93; H, 4·68; N, 5·51. $C_{15}H_{11}O_3N$ requires C, 71·14; H, 4·34; N, 5·53 per cent).

1-Naphthyl-3 : 5-o-nitrobenzylidene-2 : 4 : 6-triketopiperidine (VII, R=*o-nitrophenyl*).—An acetic acid solution of equimolecular proportions of the compound (VI) and *o*-nitrobenzaldehyde was heated under reflux for about 1 hour. On cooling a crystalline precipitate slowly separated which crystallised from glacial acetic acid in orange rectangular plates, yield 75%. It resinifies at 233-35°. (Found: N, 7·29. $C_{22}H_{14}O_5N_2$ requires N, 7·25 per cent). It is insoluble in alkali.

1-Naphthyl-3 : 5-cinnamylidene-2 : 4 : 6-triketopiperidine (VII, R= PhCH : CH).—The method of procedure was the same as in the case of the above compound. The product crystallised from a large quantity of glacial acetic acid in bright red rectangular plates, m.p. 263-64° (decomp.) It is insoluble in alkali. (Found: C, 78·19; H, 4·91. $C_{24}H_{17}O_3N$ requires C, 78·47; H, 4·63 per cent).

Ethyl 2 : 6-dicarbethoxyiminothiopyran-4-one-3 : 5-dicarboxylate (VI).—Sodium (2·3 g.) was gradually added to a solution of ethyl acetone dicarboxylate (10·2 g.) in absolute ether (200 c.c.). After the evolution of hydrogen had ceased, a toluene solution of carbethoxythiocarbimide (13·5 g., prepared according to the method of Doran, *J. Chem. Soc.*, 1896, **69**, 326) was added, when the reaction commenced at once with evolution of heat, yielding in a short time a fine yellow solid. After standing overnight, the precipitate was filtered, dissolved in water and acidified when there was evolution of sulphuretted hydrogen. The dark red viscous oil when kept in a vacuum desiccator, slowly changed into a semi-solid mass. It was twice crystallised from a mixture of benzene and petroleum ether (b.p. 75-90°) in beautiful colourless needles, m. p. 122-123°, yield 2·5 g. [Found: N, 6·67; S, 7·82; M. W. (by titration), 434. $C_{17}H_{22}O_9N_2S$ requires N, 6·51; S, 7·44 per cent. M. W., 430). It is soluble in alkali and precipitated by acids, and is not desulphurised by oxide of mercury.

My best thanks are due to Prof. P. C. Guha for his valuable criticism and kind interest in the present investigation.

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The Electrical Conductivity of Potassium Chloride in Certain Mixed Solvents.

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The object of this work was to discover whether non-electrolyte molecules possess dipole moments group themselves round the ions of an electrolyte in a solution which contains both. If any such groups are formed, the mobility of the ion will be changed. If an unsolvated ion becomes the centre of such a group, its mobility should become smaller; but a solvated ion might have its group of solvent molecules replaced by a smaller group of molecules of non-electrolyte, in which case the mobility would increase.

The substances chosen were potassium chloride as the electrolyte, and as non-electrolytes, methyl, ethyl and *iso*propyl alcohols and acetone. All these have reasonably high dipole moments and are miscible with water in all proportions. The electrical conductivity of potassium chloride in a mixture of water and each of these non-electrolytes was determined over a considerable range of concentrations, and an attempt was made to interpret the results.

The potassium chloride and acetone used were analytical reagents, and the alcohols had been purified by distillation over quicklime twice. Water for the conductivity determinations was prepared in a Hartley's still, the first and last thirds being rejected. It had a specific conductivity of 2×10^{-6} ohms^{-1}. The usual precautions were observed in storing and using all these substances. The cell was an old one of hard glass, with electrodes of bright platinum foil. (Platinized electrodes promote the atmospheric oxidation of alcohols: Partington, *J. Chem. Soc.*, 1911, **99**, 1937). The resistance was determined by means of a Pye bridge and buzzer. Temperature control was by means of a thermostat kept constant at $25° \pm 0{\cdot}1$.

Each solution was made up as follows: the required quantities of non-electrolyte and of a known concentrated solution of potassium chloride were mixed, made up to 50 c. c. by addition of water, and

transferred to the cell, which was then allowed to remain in the thermostat for twenty minutes to attain the right temperature. The resistance was then determined. When solutions in 100% non-electrolyte were possible, these were prepared separetely. Viscosities were measured with a pyknometer and Ostwald viscometer. It was found that the effect of potassium chloride was negligible when compared with that of the non-electrolytes; and viscosity-composition curves for the liquid mixtures employed were determined. The viscosity of pure water was taken to be $8{\cdot}95 \times 10^{-3}$ at 25°.

The results in the case of water-ethyl alcohol mixtures are in good general agreement with those of Walker and Hambly (*J. Chem. Soc.*, 1897, **71**, 61), whose electrolyte was diethylamine hydrochloride. This type of behaviour is well known. Complex relations in the case of water-acetone mixtures have previously been observed by Jones and Mahin (*J. Amer. Chem. Soc.*, 1909, **41**, 433;) *Z. physikal. Chem.*, 1909, **69**, 389) and other workers. Solutions of potassium chloride in these mixtures do not appear to have been investigated, nor have irregularities similar to those discussed in this paper been observed. The relevant literature is extensive, but little work on conductivity in mixed solvents has been published in recent years. Modern knowledge of dipole moments and molecular configurations should throw much light on the results of older researches.

TABLE I.

Viscosities and specific conductivities of the liquid mixtures.

% non-electrolyte	0	20	40	60	80	100
Viscosity $\times 10^3$.						
Water-MeOH	8·95	12·79	15·43	14·54	11·04	5·99
Water-EtOH	8·95	15·24	21·94	22·46	18·65	12·08
Water-acetone	8·95	12·04	13·36	12·64	7·29	3·49
Sp. conducy. $\times 10^6$.						
Water-MeOH			2·8	3·8	5·0	7·6
Water-acetone		5·66	4·04			

Where the specific conductivity is not given, it is less than $2{\cdot}8 \times 10^{-6}$, the limit set by our bridge. In the case of water-EtOH and water-PrOH mixtures, it is always less than this value. Percentage of non-electrolyte is expressed by volume.

TABLE II.

Equivalent conductivity of KCl *in aqueous alcohol.*

% of alcohol	0	20	40	60	80	90	100
			Water—MeOH				
N/10-KCl	128·9	94·8	73·2	64·4	60·8	59·6	
N/20	133·0	93·9	73·6	64·0	61·6		
N/50	138·4	96·9	75·3	66·6	65·9		75·4
N/100	141·2	102·3	81·2	70·4	72·0		80·7
N/500	146·3	104·6	81·3	74·6	76·5		95·1
N/1000	147·4	105·7	82·4	76·0	79·4		100·2
			Water—EtOH				
N/10	128·9	78·0	53·0	38·0	26·5		
N/20	133·0	81·0	54·3	40·3	29·9		
N/50	138·4	86·5	57·1	43·0	33·2	29·5	
N/100	141·2	89·1	59·1	45·2	37·1	33·7	
N/500	146·3	92·4	61·7	49·7	42·2	39·6	
N/1000	147·4	93·6	64·3	52·4	44·9	41·0	
			Water—*iso*PrOH				
N/10	128·9	78·5	48·8	29·5	17·0		
N/1000	147·4	85·3	54·0	35·8	25·9		

TABLE III.

Equivalent conductivity of KCl *in aqueous acetone.*

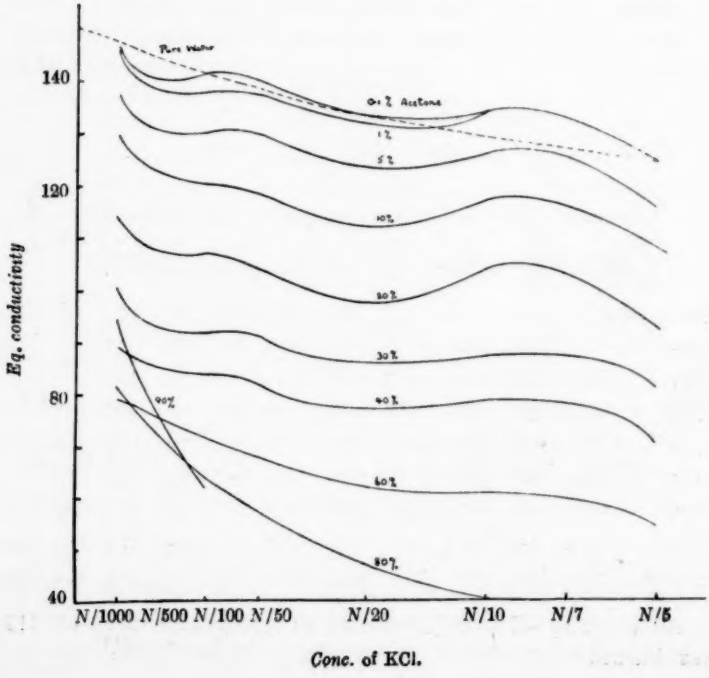
% of acetone	0	0·1	1	5	10	20	30	40	60	80	90
N/5-KCl	123·9	123·9	123·9	115·0	107·4	92·0	80·5	70·0	53·7		
N/7	127·0	132·5	132·5	125·1	115·5	102·4	86·6	77·6	59·2		
N/10	128·9	133·7	133·7	125·8	116·7	103·5	86·7	78·3	60·6	40·1	
N/20	133·0	133·0	131·5	123·2	111·6	97·0	85·7	76·9	61·7	46·6	
N/50	138·4	139·7	137·1	129·6	118·0	103·6	90·7	81·5	67·6	57·0	
N/100	141·2	141·2	137·8	130·1	120·2	106·8	91·6	83·7	71·5	63·6	61·6
N/500	146·3	141·9	140·5	132·9	125·3	108·8	94·9	86·8	77·6	77·2	84·6
N/1000	147·4	146·6	145·9	137·6	129·7	110·6	100·3	89·0	78·9	81·2	94·1

Also, for *N*/2-KCl in 1% acetone, an approximate value of 115 was obtained.

If the equivalent conductivity is plotted against the percentage of each non-electrolyte, families of curves are obtained (one curve for each concentration of potassium chloride). In every case these curves start roughly parallel and sloping steeply downwards, but as the concentration of non-electrolyte increases they slope less and tend to diverge, this effect being greatest in water-acetone, and least in water-*iso*PrOH mixtures. Minima appear in some of the water-acetone and water-MeOH curves, but they never correspond to the maximum viscosity. Irregularities also occur, while the water-EtOH and water-*iso*PrOH curves are smooth and regular. The authors are convinced, from a study of all the curves, that the variation in conductivity cannot be explained wholly, or even primarily, in terms of viscosity, as some workers have attempted to do.

FIG. 1.

Conductivity in aqueous acetone.



Now if the equivalent conductivity is plotted against the square root of the concentration of potassium chloride, other families of curves result (one curve for each non-electrolyte percentage). With pure water and water-EtOH mixtures these approximate to straight lines, indicating complete dissociation on the Debye-Hückel theory. Water-MeOH and water-acetone curves, on the other hand, show a series of regularly spaced maxima and minima (see Fig. 1). The irregularities in the other type of curve, mentioned above, are connected with these. At the higher non-electrolyte concentrations these tend to smoothe out, and the curves approximately obey Rudolphi's modification of Ostwald's equation, characteristic of incomplete ionisation.

Discussion.

Although no obvious connection exists between conductivity and viscosity, a relation is apparent between conductivity and the dipole moments of the non-electrolytes employed. The following figures are taken from Glasstone ("Recent Advances in Physical Chemistry," Chap. III).

Table IV.

Liquid	MeOH	*iso*-PrOH	EtOH	Water	Acetone
Dipole moment $\times 10^{18}$	1·64	1·70	1·72	1·60	2·71

It will be observed that those liquids, which have dipole moments near to that of water, give, when mixed with water, the most regular conductivity results, *e.g.*, EtOH and *iso*PrOH. MeOH shows a certain amount of irregularity, while acetone, whose dipole moment is very different from that of water, gives very irregular results.

From Fig. 1, it will be seen that maxima and minima occur on all but the last two curves, and always at the same concentrations of potassium chloride. The concentration of acetone appears to have no effect on their position, although some acetone must be present if they are to occur at all (0·1 % is sufficient), and too much acetone suppresses them. It is possible to calculate the average distance apart of the potassium and chloride ions in solutions exhibiting maxima and minima, taking $N = 6{\cdot}06 \times 10^{23}$; these distances are given in Table V, which also shows the average relative motions of two ions of opposite sign, calculated from potential gradients actually observed in our cell and the known mobilities of the ions.

TABLE V.

	KCl conc.	Av. distance apart of the ions.	Av. relative motion of the ions.
Minimum	0·4 *N*	12·9 Å.U.	...
Maximum	0·1156	19·26	70 Å.U.
Minimum	0·0500	25·21	140
Maximum	0·0144	38·56	280
Minimum	0·0064	50·52	360

It will be observed that the distances apart of the ions in the three solutions giving minima, are in the simple ratio of 1:2:4. In the case of the maxima, we get the ratio 1:2. The relation is exact except in the first minimum, which corresponds to an experimental result in $N/2$ solution of doubtful accuracy.

The explanation that immediately suggested itself to us was that of the formation of chains of acetone molecules between the ions, due to the alignment of acetone molecules under the influence of their dipole moments. These chains we called "dipole-association" chains; they would terminate on ions of opposite sign, and would presumably be formed most easily if the average distance between the ions, when moving freely, is equal to the length of a chain composed of an integral number of acetone molecules. They would be broken during the conductivity determinations, unless they were able to withstand the potential gradients employed, since the relative motion of the two ions at the ends of a chain is likely to be much more than twice the length of the chain (compare the figures in the last two columns of Table V).

In order to test this theory, it is necessary to know the molecular dimensions of acetone. The only measurement so far available is that of Hengstenberg and Bru (*Anal. Fis. Quim.*, 1932, **30**, 341) who found the C–C distance to be $1{\cdot}57 \pm 4$ Å.U. This was combined with the results given for formaldehyde and other simple molecules (*Annual Rep.*, 1932, **29**, 63-70) and, as in that paper, allowance was made for a "surface of influence" 0·6 Å.U. thick all round the molecules. The ionic dimensions are those obtained by use of Stokes' law (*cf.* Taylor, "Physical Chemistry," Vol. I, p. 689) and so include this surface of influence. On trial, it was found that the distances apart of ions which are separated by chains of *hydrated* acetone molecules agree quite well with the average distances apart

of the ions given in Table V, as a comparison of the figures in Table VI with those in Table V will show.

TABLE VI.

No. of acetone mol. in the chain	1	2	3	4	5	6	
Distance apart of the terminal ions	11·5	19·0	26·5	34·0	41·5	49·0	Å.U.

It will be seen that there is quite good agreement, except that the one value 38 56 in Table V is replaced by two values 34·0 and 41·5, in Table VI. It is also necessary to explain why some of these values correspond to maxima, and some to minima in the conductivity.

It is very tempting, and not at all difficult to put forward a theory in which these difficulties are explained away by means of one or two subsidiary assumptions. But there is little experimental evidence for such assumptions as yet, and authors wish first of all to extend their investigations in this field.

In conclusion, they desire to express their gratitude to Professors B. L. Vaish and H. Krall for advice and assistance freely given.

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Note on the Anomalous Redox Potentials of Sulphhydryl-Disulphide Systems.

By Joseph W. H. Lugg.

The history of this subject commences with the work of Dixon and Quastel (*J. Chem. Soc.*, 1923, **123**, 2943) who found that the following equation described the potential set up at an 'inert' electrode immersed in a solution containing RSH and RSSR,

$$E = E_0 - \frac{RT}{F} ln\,[\mathrm{RSH}] + \frac{RT}{F} ln\,[\mathrm{H^+}] \quad \ldots \qquad \ldots \quad (i)$$

Attempts to explain the anomalous redox potential have been made by these authors who suggested that the true oxidant might be something different from RSSR and that its concentration would have to be fixed by Dixon (*Proc. Roy. Soc.*, 1927, **B**, **101**, 57) who found E_0 to vary with the electrode metal, and correlating E_0 with the hydrogen over-voltage, applied Wieland's theory of hydrogen acceptors with a supposed equilibrium diffusion of hydrogen from the electrode surface; by Barron, Flexner and Michaelis (*J. Biol. Chem.*, 1929, **81**, 743) who assumed that a small constant amount of oxygen present allowed a cysteine (RSH) solution to attack a mercury surface, thereby producing a small constant quantity of a weakly dissociating compound, the mercury electrode functioning as one of the second order for RS^- ions; and by Ghosh and Ganguli (*Biochem. J.*, 1934, **28**, 381), who believed that a film of oxygen or of an oxide, present on a mercury surface, permits a reaction with RSH in solution with the formation of mercury compounds, the electrode functioning in the manner visualised by Barron, Flexner and Michaelis (*loc. cit.*).

Ghosh, Raychaudhuri and Ganguli (*J. Indian Chem. Soc.*, 1932, **9**, 43), observed that if a cystine (RSSR) solution were partially reduced electrolytically at a mercury surface, the resulting solution would set up a potential of the normal redox form at that surface. Green (*Biochem. J.*, 1933, **27**, 678) confirmed this, but found that if a new mercury electrode were introduced, the 'anomalous' potential was established, and, therefore, ascribed the 'normal'

potential to the presence of a compound at the mercury surface that was employed in the reduction. Ghosh and Ganguli (*loc. cit.*) found that the 'normal' potential was established at a mercury surface that had first been heavily polarised cathodically, and thus came to their above mentioned conclusions concerning the origin of the 'anomalous' potential, the establishment of the normal form being attributed to the use of a surface from which the oxygen or oxides had been removed.

In these attempts (except Dixon's, *loc. cit.*) to explain the 'anomalous' potential, there is required a constant concentration (or activity) in the solution, of an oxidant or of a heavy metal compound, according as to whether the electrode is visualised as functioning (*a*) as an inert electrode in a redox system, or (*b*) as a metal electrode of the second order for RS^- ions.

It may be pointed out that the required constancy in both these visualisations need apply only to the immediate neighbourhood of the electrode surface, but it is necessary to invest this region, regarded as a separate surface phase, with some peculiar properties. In case (*a*) it must be assumed that electrons only are engaged in the transfer of electricity between the metal and the surface phase, whilst ions only are so engaged between this phase and the bulk solution, and that the oxidant (possibly RS) is confined to the surface phase. In case (*b*) it must be assumed that ions of the metal are engaged in the transfer between the electrode and the surface phase but not between the surface phase and the bulk solution, and that the compound is confined to the surface phase.

The first case provides a ready explanation for the observations of Michaelis and Flexner (*J. Biol. Chem.*, 1928, **79**, 689) who, in a series of most carefully conducted experiments, found that the potential varied but little with the electrode metal (mercury, smooth platinum, and gold-platinum) and thereby dismissed Dixon's explanation (*loc. cit.*).

Actually, however, it seems that the simplest physical picture is obtained by merging the two visualisations and assuming that the RS radicles are combined with the surface metal atoms, forming a surface compound; the postulated constant activity of oxidant or compound being dispensed with altogether. It is supposed that the RS radicles are RS^- ions whose charges reside in the metal, and that in consequence of a vibrational motion, the bound ions can escape into the solution when their kinetic energy in an outward movement exceeds

a critical amount. They leave the metal with a deficiency of electrons, and equilibrium is established when the rate of loss of RS^- ions by the covered fraction of the surface equals the rate at which RS^- ions from the solution combine with the bare charged fraction. The electrode is regarded as a sort of first order ' RS electrode.'

For simplicity it is assumed that the R radicle itself has no dissociating groups, that there is no orientation of solvent molecules at the surface and the surface compound has negligible dipole moment, and that whilst all negative ions striking the bare charged surface may be held there the RS^- ions alone are bound to any appreciable extent. In order to allow for metal-metal junction potentials it is convenient to imagine the electrode metal (at electrical potential E_m) connected with some reference metal (at potential E_r). The potential difference $E_r - E_s$, where E_s is the potential of the bulk solution, is the one with which we are eventually concerned.

From Butler's (*Trans. Faraday Soc.*, 1924, **19**, 729), application of classical statistical mechanics to first order metal electrode systems the following approximate equations, (*ii*) and (*iii*), are readily developed, and Richardson's thermionic equation yields (*iv*),

$$N_1 = (n-x)\,\gamma\,\sqrt{RT/\pi W'_1}\;e^{-W'_1/RT-(E_m-E_b)F/RT} \qquad \ldots \quad (ii)$$

$$N_2 = \frac{xN_0C}{n\ 1000}\sqrt{RT/2\pi M}\;e^{-W'_2/RT-(E_s-E_b)F/RT} \qquad \ldots \quad (iii)$$

$$E_r - E_m = \frac{W_m - W_r}{F} + \frac{RT}{F}\ln\frac{k_r}{k_m} \qquad \ldots \quad \ldots \quad (iv)$$

where N_1 is the number of RS^- ions lost per second per cm.^{2} of surface, and N_2 is the number gained from the solution; γ is a mean frequency of vibration of the bound RS^- ions; R, T and F have their usual significance; E_b is the potential at the ' balance point ' at which an RS^- ion experiences equal attraction for the surface and for the solution; N_0 is Avogadro's number; M is the gram-ionic weight of the RS^- ions and C is their concentration in gram-ions per 1000 c.c.; W'_1 and W'_2 are the ' non-electrical ' fractions of the work N_0 RS^- ions must do just to reach the balance point from the surface and from the interior of the solution respectively; n is the number of RS^- ions per cm.^{2} of surface when the layer is complete, and x is the number that have left the surface; W_m and W_r are the energies absorbed in the separation of

N_0 electrons from the electrode and reference metals respectively, and k_m and k_r are constants characteristic of the metals.

At equilibrium $N_1 = N_2$, and hence from (*ii*) and (*iii*),

$$E_m - E_s =$$

$$\frac{W_2 - W_1}{F} + \frac{RT}{F} ln \frac{1000\, n\gamma}{N_0} \sqrt{\frac{2M}{W_1}} + \frac{RT}{F} ln \frac{n-x}{x} - \frac{RT}{F} ln\ C \quad \ldots (v)$$

in which $W'_2 - W'_1$ in the first term on the right has been replaced by its equivalent, $W_2 - W_1$, W_1 being the energy absorbed in the separation of N_0 RS^- ions from the surface, and W_2, the energy evolved in their hydration; and W'_1 under the root sign in the second term has been replaced by W_1 as an approximation.

One consequence of the assumptions that have been made is that the p. d. $E_m - E_s$ must rasult from the separation of the RS^- ions from the surface and hence that it could not be negative, and the Helmholtz equation gives,

$$E_m - E_s = Hdx \quad \ldots (vi)$$

where H is a constant ($1{\cdot}8 \times 10^{-6}$ volt/cm.) and d is a mean equivalent *vacuo* separation of the positive charges from the separated RS^- ions or their equivalents in the solution. Although d may vary somewhat, it will be assumed constant for the present purposes and given the value 10^{-8}cm. as representing its order of magnitude. Substituting (*vi*) in (*v*) it is seen that x increases continuously as C decreases, but it is not possible to express x or $E_m - E_s$ as an explicit function of C. From (*vi*) it is seen that an increase of 0·5 volt in $E_m - E_s$ requires an increase of about $3{\cdot}10^{13}$ in x. On the other hand, n, identified with the surface concentration of metal atoms, is of the order 10^{15}, and hence, unless x or $n-x$ were initially very small, the first three terms on the right in (*v*) could be replaced by a constant, E'_0, for any one metal over a very wide range in C.

The magnitudes of most of the quantities appearing in (*iv*) and (*v*) are either unknown or are known only approximately. The second term on the right in (*iv*) is usually considered insignificant in comparison with the first. Setting $T = 300$; $M = 100$; and (from consideration of the 'residual ray' frequencies of elements and compounds, heats of ionisation of various compounds, heats of hydration of ions,

the photo-electric effect and thermionic emission) $\gamma=10^{13}$ sec.$^{-1}$; W_1, W_2, W_m, $W_r=10^6$ joules. as possibly representing their orders of magnitude, it is found that the second term on the right in (v) is of the order $+0{\cdot}3$ volt and that its variation with the electrode metal will perhaps be slight. In as much as a large change in E_m-E_s requires only a small proportional change in x or in $n-x$ when neither of these quantities is very small, the third term on the right in (v) can perhaps likewise be expected to vary but little, and under these circumstances E_r-E_s would be substantially independent of the electrode metal if W_m-W_1 were constant. This, possibly, is not an unreasonable condition; a considerable part of W_1 must be represented by W_m, and the remainder may not vary much with similar metals.

In the simple instance dealt with in this outline of a possible mechanism for the 'anomalous' potential, the quantity C, or (without sensible error) $[RS^-]$, is related to the total RSH concentration, through the stoichiometric dissociation constant of the sulphhydryl group (k), and in place of the last two terms on the right in equation (i) there is obtained,

$$-\frac{RT}{F}\,ln\,[RSH]+\frac{RT}{F}\,ln\,[H^+]+\frac{RT}{F}\,ln\,(1+k/[H^+]).$$

If k is given the value $10^{-10{\cdot}28}$, corresponding with one of the constants obtained by Cannan and Knight (*Biochem. J.*, 1927, **21**, 1387), from electrometric titration of cysteine, the new equation fits the data of Michaelis and Flexner (*loc. cit.*) rather well. The precise significance of this agreement into a region where equation (i) fails with cysteine ($p_H > 9$), is obscure because of the presence of an amino and a carboxyl group in this compound. Barron, Flexner and Michaelis (*loc. cit.*) ascribed the departure above p_H 9 to an alteration in the composition of their postulated weakly-dissociating metal compound, whilst Michaelis and Flexner (*loc. cit.*) believed it to be associated in some way with dissociation at the sulphhydryl group.

Systems that could furnish 'anomalous' potentials in the manner outlined above are not excluded from the 'normal' redox category if electron change between their species and the electrode is precluded by formation of the surface compound. The 'normal' potential would then be established if formation of the compound were prevented and electron exchange were, at the same time, possible.

The surface compound could have its origin in a reaction of RSH with the surface metal atoms, or in dissociation of RSSR on the

surface, or in a reaction of RSH with oxygen attached to the surface. Unlike the first two, the last mentioned possibility does not accord with the work of Michaelis and Flexner (*loc. cit.*) who found excellent recovery of the 'anomalous' potential from pronounced cathodic polarisation of the electrode, nor can it be reconciled with their observation that the potential is fairly well established with a black platinum electrode that has first been saturated with hydrogen and then washed with nitrogen while immersed in the cysteine solution. In reference to the first two possibilities on the other hand, although the heavy cathodic polarisation at a mercury surface, employed in the electrolytic reduction of cystine, would presumably replace the RS radicles with a layer of hydrogen atoms, it seems rather unlikely that the layer would be sufficiently stable to permit the establishment of even a drifting potential of the normal type.

SUMMARY.

The establishment of the anomalous redox potentials of sulphhydryl-disulphide systems, is attributed to the ionisation of a surface compound, formed by the combination of RS radicles with the surface atoms of the electrode metal.

A simple theory of the 'surface compound' electrode is given.

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Parachors and Chemical Constitution. Part VI. Quadrivalent Tellurium Compounds.

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Lowry and Gilbert (*J. Chem. Soc.*, 1929, 2867 ; Sidgwick, "The Covalent Link in Chemistry." 1933, p. 206; Lowry, "Optical Rotatory Power," 1935, pp. 58-59) prepared optically active forms of phenyl-*p*-tolylmethyltelluronium iodide. This led them to conclude that quadrivalent tellurium, like quadrivalent sulphur and selenium, possesses a tetrahedral configuration.

Burstall and Sugden (*J. Chem. Soc.*, 1930, 229) determined the parachors of some diaryltellurium dihalides in the fused state. They have shown the compounds to possess a non-polar structure in which each halogen atom is linked by a single electron to the central tellurium atom, thereby completing its octet.

If these compounds do contain single electron bonds to the halogen, there should be a paramagnetic effect due to the unpaired electrons (Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 3229). Actually this will be masked by the diamagnetic effect of the rest of the molecule. However, if there is any paramagnetic effect, it will be shown by the variation of magnetic susceptibility with temperature. Bhatnagar and Labiri (Z. *Physik*, 1933, **84**, 671) examined the compounds α-Me_2-Te R_2 (R=Cl, Br, I and NO_3) and found the susceptibility to be constant up to and beyond the melting point. Assuming all the bonds to be electron pairs they calculated the susceptibilities and found that they all agreed with the observed values. Hence they concluded that there was no evidence for the single-electron bond in these compounds.

In an attempt to find the molecular structure of these diamagnetic tellurium compounds, their parachors have been determined in the fused state.

Experimental.

The tellurium compounds were prepared by the method of Vernon (*J. Chem. Soc.*, 1920, **117**, 86; 1921, **119**, 694) and their tellurium content was determined by the method of Drew and Porter (*ibid.*, 1929, 2094).

1. α-Dimethyl telluridichloride, m.p. 96° (Found: Te, 55·55. calc. Te, 55·81 per cent).

2. α-Dimethyl telluridibromide, m.p. 92° (Found: Te, 39·96. calc. Te, 40·16 per cent).

3. α-Dimethyl telluridi-iodide, m.p. 127° (decomp.). (Found: Te, 30·82 calc. Te, 30·99 per cent).

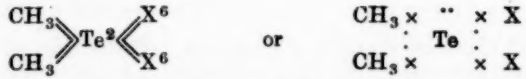
4. α-Dimethyl telluridinitrate, m.p. 142° (Found: Te, 44·80. calc. Te, 45·28 per cent.).

The densities were determined with a U-shaped pyknometer (Sugden, *J. Chem. Soc.*, 1925, **127**, 1171) and surface tension by the method of maximum bubble pressure using the apparatus described by Bhatnagar and Singh (*J. chim. phys.*, 1928, **25**, 21). The results are given in Table I.

TABLE I.

	Substance.	Temp.	Density.	Surface tension.	Parachor $P_{obs.}$
1.	α-Dimethyl telluridichloride	100°	2·118g./c.c.	43·69 dynes/cm.	277·4
2.	α-Dimethyl telluridibromide	96	2·670	42·42	303·5
3.	α-Dimethyl telluridinitrate	144	1·985	39.15	354·8

These compounds have been shown to contain no single-electron bonds (Bhatnagar and Lahiri, *loc. cit*) and moreover, the occurrence of singlet links formed of a single shared electron is very rare and such links are always very unstable (Sidgwick, "The Electronic Theory of Valency," p. 103). These compounds may be represented by the following electronic structure (*cf* Sidgwick, "The Covalent Link in Chemistry," *loc. cit.*)



This involves expansion of the valency group of tellurium to ten electrons. In Table II the parachors $P_{calc.}$ for these compounds calculated according to Sidgwick and Bayliss (*J. Chem. Soc.*, 1930, 2032) are, therefore, compared with their parachors, $P_{obs.}$, observed from the experimental data.

The data for compounds 4·5 is due to Burstall and Sugden (*loc. cit.*) and 6·7 due to Lowry and Gilbert (*loc. cit.*).

TABLE II.

	Substance.	$P_{obs.}$	$P_{calc.}$
1.	α-Dimethyl telluridichloride	277·4	274·6
2.	α-Dimethyl teluridibromide	303·5	302·0
3.	α-Dimethyl telluridinitrate	354·8	952·0
4.	α-Dimethyl telluridichloride	547·3	542·4
5.	Di-*p*-anisyl telluridichloride	663·2	660·4
6.	α-Diethyl telluridi-iodide	425·0	426·0
7.	β-Diethyl telluridibromide	377·3	380·0

Conclusion.

The parachors observed and calculated are in good agreement. This leads to the conclusion that the quadrivalent tellurium compounds possess a structure, in which the central tellurium atom is surrounded by a shell of ten electrons; four pairs of which are shared constituting four normal linkages and the fifth is a 'lone' pair. This view of expansion of the valency group beyond the normal octet in the quadrivalent tellurium compounds is further supported by the work of Simons (*J. Amer. Chem. Soc.*, 1930, **52**, 3488) in the case of tellurium tetrachloride.

The authors desire to think Prof. H. B. Dunnicliff for his interest in the work.

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Analytical Uses of Nessler's Reagent. Detection of Aldehydes. Quantitative Estimation of Glucose. Part I.

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Methods which are ordinarily used for the estimation of glucose are often found to be attended with experimental difficulties. In case of Fehling's or Pavy's method the process is not only indirect, *i.e.*, a standard solution of pure glucose is required for comparison, but invariably gives discordant results on account of the easy oxidisability of cuprous oxide which is formed. The present work was undertaken in order to simplify the process of estimation and to eliminate other attendant difficulties. Our attention was drawn to two papers by Gros and Bougault (*J. Pharm. chim.*, 1922, **26**, 5. 170), in which they made a statement that Nessler's reagent could be suitably used for the estimation of some ketones and aldehydes, as an example of which they gave details of the estimation of acetone in urine. It was thought worth investigating whether a similar process should be applicable to the estimation of glucose. According to Gros and Bougault ketones are treated with Nessler's reagent and the mixture, thus obtained, is neutralised and treated with excess of standard iodine solution when the mercury which is formed goes into solution ; the excess of iodine is then titrated back. This method

was tested with a standard solution of carefully dried purest glucose (Bacto dextrose-difco standard) and after numerous experiments conditions have been so standardised that it gives quantitative results (*cf.* Tables III and IV) using various concentrations. Comparative experiments were done with Fehling's solution (Table V) and with pathological urine (Table VI).

In order to see whether the limited observations of Gros and Bougault could be extended to all aldehydes and ketones, we repeated at first their experiments under the conditions described by them but surprisingly we have not been able to substantiate their results. For example the above authors stated that acetone, methyl-ethyl ketone, *cyclo*hexanone trimethyl*cyclo*hexanone, acetophenone, *p*-methoxyacetophenone reduced alkaline Nessler's reagent, whereas we found negative results in all cases.

It has been furthur found after experiments with numerous aldehydes and ketones that in general, ketones do not reduce alkaline Nessler's solution but aldehydes do (*cf.* Table I). In view of striking discrepancy of our results from those of Gros and Bougault we repeated our results several times with carefully purified substances but we could not corroborate them in any case. In the course of the experiments several exceptions (which can be otherwise explained) have been found (*cf.* Table II).

(1) Hydroxyaldehydes do not reduce but when the OH-group is protected usual reduction occurs.

(2) Hydroxyketones like benzoin and fructose reduce.

It has been found that K_2HgI_4 in strongly alkaline medium is easily and rapidly reduced. The strength of alkali is an important factor in the case of the reduction of the reagent with glucose or fructose. The extent of reduction depends on the strength and nature of the alkali (NaOH, KOH or Na_2CO_3) and temperature of the reaction. Thus it has been found that if 10% NaOH solution be used and the reactants are heated, the oxidation of glucose and fructose proceeds to an extent equivalent to the absorption of 5 atoms of oxygen per molecule of the sugar taken. On the contrary, if 10% Na_2CO_3 solution be used, the oxidation of glucose corresponds to the absorption of 2 atoms of oxygen, but that of fructose proceeds still further.

Experimental.

The Nessler's reagent used had the composition: $HgCl_2$ (2·5 g.), KI (8 g.), water (100 c.c.), NaOH (50 c.c., 30%). A few drops of

the substance to be tested were taken in a test tube and 1 c.c. of the reagent was added and gently heated if necessary. The following table gives the results with aldehydes and ketones.

TABLE I.

Substance.	Observation.	Temp.	Substance.	Observation.	Temp.
Formaldehyde	Reduction is rapid from red, yellow and then into black.	Takes place in the cold.	Furfuraldehyde	Red to black	Cold.
			Cinnamic aldehyde	Yellow to black	,,
Acetaldehyde	,,	,,	Benzaldehyde	Red to black.	,,
Propyl aldehyde	Rapid reduction into Hg.	,,	o-Nitrobenzaldehyde	,,	,,
Aldehyde-C_8	Reduction into black Hg.	Facilitated if gently heated.	m-Nitrobenzaldehyde	,,	,,
			p-Nitrobenzaldehyde	,,	,,
			Paraldehyde	,,	,,
Aldehyde-C_9	,,	,,	Acetone	No reduction.	Hot or cold.
Aldehyde-C_{10}	,,	,,			
Aldehyde-C_{11}	,,	,,	Methylethyl ketone	,,	,,
Aldehyde-C_{12}	,,	,,	Acetophenone	,,	,,
Glyoxal	Reduction from red to black.	In the cold.	Benzophenone	,,	,,
			*cyclo*Hexanone	,,	,,
Chloral hydrate	,,	,,			
Heliotropin	Yellow, red, black.	,,			

The following table gives the results of exceptional cases with aldehydes and ketones.

TABLE II.

Substance.	Observation.	Temp.
Salicylaldehyde	Does not reduce.	Neither in the hot nor in the cold.
Vanillin	,,	,,
Anisaldehyde	Red to black.	In the cold.
Veratric aldehyde	,,	,,
Fructose	,,	,,
Benzoin	,,	,,

Estimation of glucose.—Glucose solution (standard 10 c.c.) was mixed with K_2HgI_4 solution (35 c.c.) contained in a litre flask and then 50 c.c. of Na_2CO_3 solution (10%) were added. The mixture was slowly heated, when the reduction soon commenced. The heating was continued to boiling until the whole liquid became clear and a black precipitate was found to settle at the bottom of the flask. The flask was then removed, the solution cooled and acidified with glacial acetic acid

(15 c.c.). Then 25 c.c. of $N/10$-iodine solution were added and the contents of the flask were thoroughly shaken until the finely divided black precipitate completely dissolved. The excess of iodine was then titrated by $N/10$-thiosulphate. The actual titration figures are given below

TABLE III.

1·6356 G. of glucose dissolved in 250 c.c. of water and 10 c.c. taken in each case.

0·803 $N/10$-iodine solution added.	0·943 $N/10$-hypo required.	Found.	Glucose taken.	Error.
25 c.c.	5·95 c.c.	1·6356	1·6278	0·48%
25	5·9	1·6356	1·6337	0·1
25	5·9	1·6356	1·6337	0·1
25	6·0	1·6356	1·6220	0·8

The method is being extended to the estimation of sucrose and other disaccharides.

TABLE IV.

(K_2HgI_4 *method*).

Strength per litre.	Comp.	Volume taken.	I_2-soln. added.	$N/10$-Hypo required.		Glucose in the solution. (A − B) × 0·0045.	Actual wt. of glucose present in the soln.
				Before oxidation (A).	After oxidation (B).		
21·4336 g.	2·1433%	5 c.c.	50 c.c.	47·4 c.c.	23·6 c.c.	0·1071 g.	0·10716 g.
0·8572	0·0857	25	25	23·7	18·93	0·02146	0·02143
1·7144	0·1714	25	25	23·7	14·2	0·04275	0·04286
2·5720	0·2572	10	25	23·7	18·0	0·02565	0·02572
0·4286	0·0428	25	25	23·7	21·31	0·01075	0·01071
0·2143	0·0214	25	25	23·7	22·51	0·005355	0·005358

TABLE V.

(Fehling's solution with methylene blue as internal indicator).
1 c c. Fehling's soln. = 0·001543 g. of glucose.

Strength per litre.	Comp.	Fehling's soln.	Sugar soln. required.	Sugar calc.	Sugar present (Actual amount).
21·4336 g.	2·1433%	75 c.c.	5·4 c.c.	0·1157 g.	0·11574 g.
			5·4	0·1157	
0·8572	0·0857	25	45·8	0·03920	0·03858
			45·5	0·03880	
			46	0·03940	
1·7144	0·1714	25	23	0·03943	0·03858
			23·5	0·04000	
			23	0·03943	
0·4286	0·0428	10	38	0·01628	0·01543
			37	0·01586	
			37	0·01586	
0·2143	0·0214	5	40	0·008573	0·007715
			40	0·008573	
			39	0·008359	

TABLE VI.

Analysis of sugar in normal urine with glucose by K_2HgI_4 *method.*

100 C.c. urine contains 0·7980 g. of glucose.

Volume of urine solution taken.	Iodine solution added.	0·7587 *N*/10-Hypo required. Before oxidation (A).	After oxidation (B).	Glucose in the urine soln. (A − B) × 0·7587 × 0·0045.	Actual glucose in urine soln.
5 c.c.	25 c.c.	31·25 c.c.	19·6 c.c.	0·0398	
5	25	31·25	19·6	0·0398	0·0399
5	25	31·25	19·65	0·0396	

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Kinetics of Reactions in Heterogeneous Systems. Part I. The Reaction between Carbon Disulphide and Alkali.

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Investigations on the kinetics of liquid heterogeneous reactions are rare. Each reaction in the liquid-liquid system appears to have its own special characteristic and the measurement of the velocity is, in many cases, complicated by side reactions.

Carrarra and Zoppelari (*Gazzetta*, 1894, **24**, 364; 1896, **26**, 483) investigated the reaction between water on the one hand and sulphuryl chloride, thionyl chloride, phosphorus trichloride, phosphorus tribromide and phosphorus oxychloride on the other. Goldschmidt and Messerschmidt (*Z. physikal. Chem.*, 1899, **31**, 235) have studied the reaction of ethyl acetate dissolved in benzene with aqueous hydrochloric acid. They assumed that (*i*) the ester diffused very rapidly in both the phases, and (*ii*) that the reaction took place only in the aqueous phase. They showed that the monomolecular formula could be applied with a small correction for the counter reaction. Kremann investigated the hydrolysis of *iso*amyl acetate and of ethyl benzoate (*Monatsh.*, 1903, **26**, 315) and concluded that the velocity of the reaction, in the aqueous layer, is determined solely by physical factors like solubility, etc. A generally applicable rule for such reactions is thus not possible. Goldschmidt (*Z. Electrochem.*, 1900, **11**, 430), however, considers that the aqueous phase is saturated from the very beginning on account of the continuous agitation of the reaction mixture and that the velocity can be represented as that of an ordinary bimolecular reaction, or, if one of the reactants is present in excess, as that of a monomolecular reaction.

A large number of investigations * deals with the relation between the velocity and the rapidity of agitation (shaking or stirring).

* Sakurda (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928 **8**, 21,); Fraenkel, Wengel and Cahn (*Z. anorg. Chem.*, 1928 **171**, 82); Bell (*J. Phys. Chem.*, 1928, **32**, 892); Strauss and Hussey (*Ber.*, 1909, **42**, 2168); Titani and Kuran o (*Bull. Soc. Chem. Japan*, 1931 **6**, 152); Schwab and Knoell (*Z. physikal. Chem.*, 1930, **147**, 38); Klein (*Rocz. Chem.*, 1925, **5**, 101).

Reid and his co-workers (*Ind. Eng. Chem.*, 1923, **15**, 1048; 1926, **18**, 535) have carried out important experiments in this connection.

We have investigated the reaction between carbon disulphide and alkali with and without non-aqueous solvents for the former, and also studied the effect of an addition of hydrogen peroxide on the velocity. The velocity of this kind of heterogeneous reaction must be divided into three parts, (*i*) the homogeneous reaction between the dissolved carbon disulphide and alkali; (*ii*) reaction between the undissolved carbon disulphide and the alkali at the surface of contact; and (*iii*) the reaction between the vapour of carbon disulphide and the aqueous alkali. In case no solvent is used for the carbon disulphide, the homogeneous reaction depends on the solubility in water of carbon disulphide and in case a solvent is used, on the distribution coefficient of carbon disulphide between the solvent and water. The second, *i.e.*, the liquid heterogeneous part of the reaction will further depend on the speed with which the resulting reaction products are removed from the surface of contact into the interior of the aqueous phase and the reactants brought from the interior to the surface of contact. The third part may be supposed to depend only on the speed of shaking and the alkali concentration, provided there is enough carbon disulphide to saturate the empty space in the bottle. Moreover, if one of these processes is very much slower than the others, it will be the factor on which the reaction velocity will mainly depend.

Experimental.

Procedure.—The reactants were mixed together in glass bottles shaken mechanically inside a cellar, where the temperature did not vary more than 0·1°. After a certain time the two layers in the reaction mixture were separated and the amount of combined sulphur present in the aqueous layer, which was a measure of the amount of reaction, was determined quantitatively. The quantitative analysis of the free and combined sulphur in the aqueous layer was carried out by the following method:

A known quantity of the separated aqueous layer was mixed with some fairly concentrated alkali solution in a beaker of about 400 c. c. capacity. (In case the alkali used in the experiment was concentrated enough, this addition is not necessary.) Bromine was then gradually added until a slight colouration was obtained and the oxidation was then carried to completion by the addition of concentrated nitric acid,

keeping the beaker cooled by means of cold water throughout the process. The excess of nitric acid was then driven off, in the usual way, the residue dissolved in water, a little hydrochloric acid and ammonium chloride added and sulphur estimated as barium sulphate. In the tables that follow, the carbon disulphide used up represents the amount thus obtained.

Solubility of carbon disulphide.—Solubility of pure carbon disulphide was determined in double distilled water at 26° and the value obtained 0·1634 g. in 100 c.c. of solution agrees well with that found by Rex (*Compt. rend.*, 1884, **99**, 892, ; 1885, **100**, 773).

The solubility of carbon disulphide in solutions of sodium chloride of different concentrations at 26° was also determined. The following table gives the results.

TABLE I.

Normality of NaCl soln. ...	0·0	0·5	1·0	1·5	2·0	2·5
Solubility of CS_2 ...	0·1634	0·1331	0·1115	0·0947	0·0832	0·0753
(g./100 c.c. soln.)						

Calculation of velocity constant.—In order to determine the velocity constant, the infinity values in the case of the reaction between carbon disulphide and sodium carbonate, as well as hydroxide, were determined. As the carbon disulphide was always in excess, we found by trial that 50·0 c. c. of *N*-NaOH used up 0·881 g. of CS_2.

Speed of shaking.—The speed of shaking was controlled by interposing a variable resistance before the shaking motor and three readings were taken, the speed being given in revolutions per minute One revolution of the wheel is equal to one to-and-fro oscillation of the bottle. The same bottle was used for all the three experiments.

TABLE II.

N-NaOH = 50 c.c. CS_2 = 6·315 g. (5 c. c.). Time = 1 hr. Temp. = 24·6°.

Speed (R. P. M.) ...	129·5	147·5	164·6
CS_2 used up (%) ...	3·207	3·794	3·977

It can be easily observed here that the increase is not directly proportional to the speed, the ratio of speed to the extent of reaction diminishing with increasing speed. No definite numerical relationship between the amount of reaction and the speed of shaking can, therefore, be deduced.

Temperature.—The speed here was kept constant.

TABLE III.

Amounts of reactants and time, same as in Table II.

Temp. ...	29°·0	31°·0	33°·5
CS_2 used up % ...	5·137	5·946	7·160

The increase in the extent of the reaction is seen to be nearly proportional to the rise in temperature and is approximately 8% per degree; the decrease in solubility of carbon disulphide on rise in temperature has the effect of diminishing the temperature coefficient (Chancel and Parmentier, *loc. cit.*).

Total volume of the liquid.—The experiments were performed in three groups by varying the amounts of sodium hydroxide. Although the temperature differed for different groups it was constant for the experiments in one group. The speed of shaking was also kept constant. Amount of carbon disulphide and time are same as in Table II. Amounts in columns 2, 4 and 6 are intended to give an idea of the reaction per unit volume.

TABLE IV.

Temp. = 25°·20.			Temp. = 25°·7.			Temp. = 26°·5.		
NaOH used.	$BaSO_4$ from 1 c.c. of aq. phase.	% of CS_2 used up.	NaOH used.	$BaSO_4$ from 1 c.c. of aq. phase.	% of CS_2 used up.	NaOH used.	$BaSO_4$ from 1 c.c. of aq. phase.	% of CS_2 used up.
10 c.c.	0·03860 g.	0·9972 g.	30 c.c.	0·03196 g.	2·477 g.	50 c.c.	0·02849 g.	3·681 g.
20	0·03528	1·854	40	0·03194	3·301	100	0·02663	6·884
30	0·03512	2·723	50	0·03189	4·129	150	0·02564	9·940
			60	0·03168	4·911	200	0·02037	10·52

It is observed here that the total amount of reaction increases according to the increase of the amount of sodium hydroxide, the rate of shaking remaining constant.

The extent of the surface of contact will become smaller when the volume of alkali used goes beyond a certain limit on account of the smaller empty space available in the vessel. On the other hand, the

speed with which the reactants reach the surface of contact may be expected to increase on account of the increased total volume. The two effects are thus opposed to each other and the first is evidently more than compensated by the second, showing a net increase in the total amount of the reaction.

Concentration of alkalis.—In order to ascertain the relation between the concentration of alkali used and the extent of reaction, sodium hydroxide solutions of varying concentrations were shaken with carbon disulphide for different periods. The temperature was constant for one single group of experiments but differed for the three sets by one or two degrees.

TABLE V.

Sodium hydroxide

Amounts of reactants same as in Table II.

Time = 1 hr. Temp. = 25°		Time = 1 hr. Temp. = 25°		Time = 2 hrs. Temp. = 22°		Time = 3 hrs. Temp. = 24°	
NaOH.	% of CS_2 used up.	NaOH.	% of CS_2 used up	NaOH.	% of CS_2 used up.	NaOH.	% of CS_2 used up.
0·1*N*	0·7127	0·5*N*	2·288	0·1*N*	1·003	0·1*N*	1·111
0·2	1·136	0·6	2·622	0·2	1·681	0·2	2·113
0·3	1·539	0·7	2·901	0·3	2·317	0·3	2·971
0·4	1·932	0·8	3·231	0·4	2·945	0·4	3·852
		1·0	3·841	0·5	3·526	0·5	4·666
				0·6	4·035	0·6	5·479
				0·7	4·423		

TABLE VI.

Potassium hydroxide.

Amounts of reactants same as in Table II. Temp. = 21·5°. Time = 1 hr.

N-KOH ...	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
% of CS_2 used up ...	0·4597	0·8401	1·155	1·472	1·763	2·040	2·303	2·583	2·893	3·221

The results in the Tables V and VI show that the strength of alkali has a great influence on the reaction. For a change of concentration in sodium hydroxide from 0·1 to 0·28*N*, the extent of reaction is doubled, for a change from 0·1*N* to 0·7*N* it is four times and so on. The increase in the amount of reaction is seen to be proportional to the increase in the concentration of alkali solution.

Concentration of carbon disulphide.—Solutions of various concentrations in petroleum (b. p. 100°) were shaken with sodium hydroxide. The volume of the solution was 25 c.c. in all experiments. The volume of alkali was 50 c.c. of *N*-NaOH and the reaction was carried out at 27° for 1 hour.

TABLE VII.

Normality of CS_2 ...	0·9387	1·785	2·573	3·217	3·834	4·399
% of CS_2 used up ...	5·745	3·606	2·834	2·442	2·096	1·823

It has been already recorded by Sakurda (*loc. cit.*) that the surface exposed is proportional to the concentration of the reactants in heterogeneous systems. That conclusion is supported by the above results. The reaction however, is not directly proportional to the concentration of carbon disulphide. As the concentration of carbon disulphide increases, the actual amount used up also increases (although not proportionately), the percentage of the carbon disulphide used up as calculated from its total quantity present, however, diminishes with increasing concentrations. This is probably due to a greater consumption of sodium hydroxide with higher concentrations of carbon disulphide and consequently a rapid decrease in the strength of alkali. The decrease in the strength of alkali is greater, the higher the concentrations of carbon disulphide.

Change in the position of the vessel.—Two bottles of the same shape and capacity were taken of which one was kept vertical and the other horizontal in the shaking machine.

TABLE VII.

Amounts of reactants, same as in Table II.

Position of bottle.	% of CS_2 used up.
Horizontal	4·205
Vertical	4·003

These experiments prove that in this particular type of shaking, the agitation is more vigorous in the horizontal position of the bottle.

Quantity of carbon disulphide.—Varying amounts of carbon disulphide from 0·1 c.c. to 10 c.c. were shaken with alkali. The experiments were carried out in two groups, the one group consisted of readings from 0·1 c.c. to 0·6 c.c. of carbon disulphide and other from 1·0 c.c. to 10 c.c. The temperature, the speed of shaking and the amount and concentration of the alkali were kept constant throughout one group of experiments.

TABLE VIII.

Amount of sodium hydroxide and time same as in Table II.

Temp. = 22·3°. Speed = 145 R. P. M. (average).			Temp. = 28·1°. Speed = 165 R. P. M. (average).		
Total CS_2.	CS_2 used up.	% of CS_2. used up.	Total CS_2.	CS_2 used up.	% of CS_2. used up.
0·1 c.c.	0·06987 c.c.	55·33	1·0 c.c.	0·3421 c.c.	27·08
0·2	0·1265	50·10	2·0	0·3469	13 73
0·3	0·1864	49·20	3·0	0·3510	9 264
0·4	0·1886	37·33	4·0	0·3550	7·026
0·5	0·1907	30·21	5·0	0·3595	3·655
0·6	0·1932	25·48	10·0	0·3654	2·894

The first three readings of the above table (column 2) show a rapid rise in the reaction from the addition of 0·1 c.c. to 0·3 c.c. of carbon disulphide. From the solubility of carbon disulphide in water, it is obvious that up to this point the reaction is a purely homogeneous one. With further addition of carbon disulphide, however, the aqueous layer becomes saturated and the two heterogeneous reactions (liquid – liquid and liquid – gas) also start. The above table shows that the heterogeneous parts of reaction do not consume any very large quantity of carbon disulphide and that the major part of the reaction takes place in the homogeneous system. Similarly, from the readings of the next group we can conclude that the addition of a large quantity of carbon disulphide does not influence the reaction to any very great extent. The homogeneous part of the reaction is evidently independent of the quantity of carbon disulphide if the latter is greater

than 0·3 c.c. It will then only depend upon the temperature at which the reaction is carried out. This may be one of the reasons of the sudden rise of the reaction velocity with a rise in temperature.

Addition of a neutral electrolyte.—The electrolyte used was sodium chloride. As the quantities of sodium chloride solution added were to be small, a 5*N* solution of the same was prepared. Similarly, the sodium hydroxide solution used was of 1·25*N*. The quantities used were adjusted in such a way that the ultimate quantity of sodium hydroxide used was 50 c.c. of 1·0*N* solution and the total volume of the aqueous phase was 50 c.c. In each case the experiment was performed in duplicate.

TABLE IX.

Amount of carbon disulphide and time same as in Table II.

Temp. = 23·5°. Speed = 139·3 R. P. M.			Temp. = 24·1° Speed = 146·6 R. P. M.		
Normality of NaCl.	CS_2 used up.	% of CS_2 used up.	Normality of NaCl.	CS_2 used up.	% of CS_2 used up.
0·0	0·2404 c.c.	3·807	0·0	0·2616 c.c.	4·143
0·2	0·2229	3·530	0·2	0·2417	3·828
0·4	0·2126	3·367	0·4	0·2299	3·642
0·6	0·2007	3·179	0·6	0·2187	3·463
0·8	0·1937	3·069	0·8	0·2071	3·280
1·0	0·1852	2·934	1·0	0·1963	3·110

The decrease in the reaction is seen to be proportional to the amount of sodium chloride added. The decrease is, as expected, due to the diminution of solubility of carbon disulphide in the aqueous phase.

Influence of addition of H_2O_2 *with constant concentration of* NaOH.—It appears from Table X that the effect of the addition of hydrogen peroxide to the reaction mixture is to increase the velocity of the same. This is probably due to the oxidation of some of the products of the reaction which decreases their concentration near the surface of contact. It is, therefore, equivalent to the carrying off of these products of reaction away from the surface of contact into the

interior of the aqueous phase. It was observed that, carbon disulphide and hydregn peroxide alone do not react with each other. The addition of varying quantities of this substance to the reactants, increases the velocity of reaction in proportion to its concentration. With higher concentrations of hydrogen peroxide, the amount of alkali used up is quite considerable. This brings about a fall in the extent of reaction in the later stages.

Influence of addition of H_2O_2 with varying concentrations of both reacting substances has been shown in Table XI.

TABLE X.

Amounts of reactants and time, same as in Table II.

Temp. 23°·9. = Speed about 137 R. P. M.

H_2O_2(*N*) ...	0·0	0·08	0·16	0·24	0·32	0·40
CS_2 used up (c.c.) ...	0·2497	0·3701	0·5153	0·6292	0·7094	0·7771
% of CS_2 used up ...	3·955	5·862	8·081	9·965	11·24	12·31

TABLE XI.

Amounts of reactants and time, same as in Table II. Temp. = 29°.

NaOH conc.	H_2O_2 conc.	CS_2 used up.	% of CS_2 used up.
1·0*N*	0·0 *N*	0·3260 c.c.	5·17
0·909	0·045	0·3397	5·37
0·833	0·083	0·3728	5·89
0·769	0·115	0·4050	6·64
0·714	0·143	0·4283	6·77
0·660	0·166	0·4580	7·24

In general we can say that the action of hydrogen peroxide is proportional to the concentration used.

Comparison of the extent of reaction with sodium and potassium hydroxides.—Normal solutions of sodium and potassium hydroxides were shaken with carbon disulphide.

TABLE XII.

Amount of reactants and time, same as in Table II. Temp. = 26·8°.

Alkali hydroxide.	CS_2 used up.	% of CS_2 used up.
Sodium	0·4788 c.c.	7·584
Potassium	0·5338	8·458

As is usual in generally all the reactions, potassium hydroxide seems to be more active than sodium hydroxide under the same conditions.

TABLE XIII.

Reaction between CS_2 in various solvents and aqueous NaOH.

Amounts of reactants and time same as in Table II. Volume of solvent = 10 c. c.

Solvent.	B.p.	Sp. gr. at 25°.	CS_2 used up.
Petroleum ether	45°	0·670	5·981 %
Petroleum	100°	0·754	5·934
Toluene	110°	0·858	8·817
Xylene	138°	0·859	6·711
Monochlorobezene	132°	1·1042	6·119
Monobromobenzene	155°	1·4856	5·654

TABLE XIV.

Comparison of the influence of concentration of carbon disulphide.

Amounts of reactants and time, same as in Table II. Volume of solvent = 25 c.c. Petroleum and xylene were used as solvents.

CS_2 normality.	Petroleum at 25° CS_2 used up.	Xylene at 27° CS_2 used up.
0·9387 *N*	5·715 %	6·764 %
1·785	3·606	4·338
2·573	2·834	3·343
3·217	2·442	2·746
3·834	2·096	2·334
4·399	1·823	2·004

The increase in the amount of reaction due to an increase in concentration is similar in both cases.

Velocity of Reaction between Carbon Disulphide and Alkali.

TABLE XV.

Carbon disulphide and aqueous sodium hydroxide.

Amounts of reactants same as in Table II. Temp. = 24·3°.
$a = 5{\cdot}400$ g. $BaSO_4$.

Time.	Wt. of $BaSO_4$ x.	Wt. of CS_2 used up.	$a-x$.	K.
60 min	1·1595 g.	0·1892 g.	4·2405	0·00175
120	1·8815	0·3070	3·5185	0·00155
180	2·5290	0·4125	2·8710	0·00152
240	2·9915	0·4881	2·4085	0·00146
300	3·2715	0·5500	2·1288	0·00135
360	3·5135	0·5782	3·5135	0·00127

'a' represents the total concentration of the alkali in 50 c.c. of normal solution in terms of barium sulphate in g.

The quantity of carbon disulphide employed was in sufficient excess since the 50 c.c. of N-NaOH would use up only 0·881 g. of CS_2. When the monomolecular formula is used for calculating the velocity constant, we get decreasing values of K.

TABLE XVI.

Carbon disulphide and potassium hydroxide.

Amounts of reactants, same as in Table II. Temp. = 24·7°.
Speed = about 150 R. P. M. $a = 5{\cdot}4$ g. of $BaSO_4$.

Time.	Wt. of $BaSO_4$ x.	$a-x$.	K.
60 min.	1·6985 g.	3·7015	0·00273
120	2·6345	2·7655	0·00242
180	3·3122	2·0878	0·00229
240	3·8150	1·5880	0·00222
300	4·0575	1·3425	0·00201
360	4·1695	1·2305	0·00178

Here also the monomolecular formula is not applicable, indicating that the reaction is more complex.

Velocity of reaction between carbon disulphide and sodium carbonate.—Normal solutions of sodium carbonate were shaken with carbon disulphide for different periods and the value of K calculated. The values of K were seen to diminish rapidly on applying the monomolecular formula as in the case of the alkali hydroxides. The same thing happened when monochlorobenzene was used as solvent for CS_2 and NaOH was used as the alkali.

Carbon disulphide and sodium hydroxide with addition of hydrogen peroxide.—Dilute peroxide solutions of less than 0·5N strength were used. This presented deposition of sulphur., 40 c.c. of aqueous sodium hydroxide of 1·25N strength were taken and mixed with 10 c.c. of the above solution of hydrogen peroxide. The resultant normality of sodium hydroxide solution was 1N, and that of hydrogen peroxide 0·1N, the total volume of the aqueous phase being 50 c.c.

TABLE XVII.

CS_2=6·415 g. (5 c.c.). Temp.=27·8°. Speed=140 R.P.M.
a=6·1 g. of $BaSO_4$.

Time.	$BaSO_4$.	$a-x$.	K.
60 min.	2·070 g.	4·030	0·00300
120	3·655	2·945	0·00230
180	3·605	2·495	0·00216
240	4·020	2·080	0·00195
300	4·347	1·753	0·00181
360	4·596	1·504	0·00172

Here also the values of K calculated by the monomolecular formula diminish regularly. But the decrease becomes smaller and smaller as the reaction proceeds.

CONCLUSION.

It has been shown in the above experiments that in the case of the system between carbon disulphide and aqueous alkali, the velocity is dependent on the following factors:—

(1) Speed of agitation, (2) temperature, (3) total volume of liquid, (4) concentration of the alkali, (5) concentration of carbon disulphide when a solvent is used, (6) quantity of carbon disulphide (when no solvent is used).

Agitation has a two-fold influence, firstly that of increasing the surface of contact (and therefore increasing indirectly the effective velocity of reaction), and secondly of increasing the velocity with which products formed are removed from and fresh reactants brought to the surface of contact.

The velocity also depends on the method of shaking and the position of the vessel. The temperature coefficient, is rather high and corresponds to about 8 per cent. per degree rise in temperature.

Increase in the total volume of the alkali, the volume of the vessel remaining constant, decreases the empty space above the liquids. But this factor is apparently more than compensated by the increase in the speed with which the products are removed from and fresh reactants brought to the surface of contact, and also by the increase in the homogeneous part of the reaction, due to the larger quantity of carbon disulphide dissolved in the aqueous phase. Thus we have a net increase in the total amount of reaction. Increase in the concentration of the alkali causes a proportionate increase in the velocity of reaction. But the increase in the concentration of carbon disulphide (dissolved in an insoluble and neutral solvent) does not increase the reaction proportionately, for the higher concentration of carbon disulphide now uses up greater quantities of alkali and the concentration of the latter falls very quickly.

Increase in the quantity of carbon disulphide used has very little influence on the velocity of this reaction, for major part of the reaction takes place in the aqueous phase which is already saturated.

Potassium hydroxide is seen to be more active than sodium hydroxide under the same conditions.

The addition of a neutral electrolyte like sodium chloride decreases the reaction velocity, by decreasing the solubility of carbon disulphide. The heterogeneous part of the reaction is not affected.

When solvents are used for dissolving the carbon disulphide, the amount of reaction is seen to vary with the solvent. The reaction goes on diminishing in the order, xylene, monochlorobenzene, petroleum ether, petroleum, toluene, and monobromobenzene. This difference is not due to any one single physical property of the solvent. It may be due, among other things, to the partition coefficient of carbon

disulphide in the two solvents, and perhaps to the viscosity an ddensity of the solvent which would determine the effect of agitation. Similarly it is observed that the change in the concentration of carbon disulphide in different solvents has the same effect on the reaction.

Addition of hydrogen peroxide increases the velocity by causing an increase in the velocity of diffusion of the reaction products into the interior of the aqueous phase. The action of hydrogen peroxide is proportional to its concentration, provided this latter is not excessive.

The reactions between carbon disulphide and aqueous sodium hydroxide, potassium hydroxide and sodium carbonate do not obey law for monomolecular reaction when one of the reactants, namely carbon disulphide is in excess. Nor is the bimolecular formula applicable when the reaction is carried out with varying finite concentrations of both the reactants. The value of the velocity constants are seen to diminish regularly. The reaction is, therefore, a complex one as is also to be expected from the complex value of the products. On the addition of hydrogen peroxide, the values of K diminish to a very small extent to become nearly constant as the reaction proceeds further and further.

The reaction can be divided into three parts, *viz.*, (1) homogeneous reaction due to the appreciable solubility of carbon disulphide in water ; (2) the heterogeneous reaction at the surface of contact of liquid carbon disulphide and aqueous alkali; (3) and the heterogeneous reaction at the surface of contact of gaseous carbon disulphide and aqueous alkali. It is observed in the previous experiments that the major part of the reaction is due to (1). The reaction, therefore, is not so sensitive to agitation as a purely heterogeneous one would be. So also the temperature effect is partly neutralised by the decrease in solubility of carbon disulphide in the aqueous phase thus decreasing the reaction in the homogeneous system.

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Kinetics of Reactions in Heterogeneous Systems. Part II. The Reaction between Benzoyl Chloride and Water.

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In the previous part (p. 719) we have investigated the reaction between carbon disulphide and alkali under different conditions. A considerable part of that reaction takes place in the homogeneous system owing to the appreciable solubility of carbon disulphide in water at the ordinary temperature. The reaction between benzoyl chloride and water is on the other hand a completely heterogeneous reaction, as benzoyl chloride is practically insoluble in water. It has, therefore, to be assumed that the hydrolysis takes place only at the surface of contact and that the resulting substances diffuse away from, and the reacting substances diffuse towards, the surface of contact between the two phases. The equation representing the reaction is as follows:

$$C_6H_5COCl + H_2O = C_6H_5COOH + HCl$$

The velocity of decomposition of benzoyl chloride in ethereal solution by water was investigated by Strauss and Hussey (*Ber.*, 1909, **42**, 2168). Their conclusions are, however, restricted to the comparative activity of the COCl group in various substituted benzoyl chlorides.

Experimental.

As the above equation shows, the acids are produced in the reaction mixture, out of which benzoic acid is very slightly soluble in water at the ordinary temperature. The separation of the solid acid, therefore, introduces a third phase into the reaction mixture and makes the reaction much more complicated. In order to avoid this, the benzoyl chloride was always dissolved in a neutral solvent not soluble in water and capable of dissolving the separated benzoic acid.

After a number of trials we found that a concentration of 0·862*N* (121·2 g. or 100·00 c.c. benzoyl chloride per litre) was sufficient to keep the benzoic acid completely dissolved throughout the course of the experiment. 10 C.c. of this solution were usually shaken with 50 c.c. of water. We found also that small differences in the nature of the internal surface of the container introduced considerable differences in the amount of the hydrolysis and the same applied also to the shape. The flasks and bottles were, therefore, so chosen that they gave identical results under identical conditions of experimentation. The shaking machine was so constructed that the conical flasks could be fastened on the platform of the same and a uniform to-and-fro movement was obtained. Conical flasks showed themselves to be capable of yielding more uniform and reproducible results.

The benzoyl chloride was allowed to stand for two days over potassium carbonate and then distilled. It was then stored in brown stoppered bottles and the stoppers smeared with pure vaseline.

The method of estimating the amount of reaction was so chosen as to give an idea of the quantity of hydrochloric acid liberated.

In the method employed (Lang and Messinger's method, *Ber.*, 1923, **53**, 14, 29) diphenylamine was used as absorption indicator. The indicator was freshly prepared for each titration by mixing 1% solution of diphenylamine in concentrated H_2SO_4 with 1 c.c. of 0·1/*N*-$K_2Cr_2O_7$ and 10 c.c. of 4−5*N* H_2SO_4. The separated water layer was taken in a flask and the indicator added. The mixture was then titrated with the silver nitrate solution. The precipitate, being in an acid solution, is coloured dark green, while the top portion has only a light green colour. The end-point shows a sudden change of colour in the top layer to violet. We found that it was necessary to add one drop of indicator for each 3 c.c. of the decinormal silver nitrate solution required in the titration.

The effect of the change in a number of different factors on the amount of benzoyl chloride hydrolysed was investigated The results are given below.

Speed of shaking.—As the system is very sensitive to change in speed, this factor was studied in great detail.

TABLE I.

Effect of speed on the extent of reactions.

Volume of water = 50 c.c. Time = 30 min. Amount of 0·8626*N* soln. of benzoyl chloride used = 10 c.c. Vol. of soln. used for estimating the amount of hydrolysis = 10 c.c.

Benzoyl chloride in monochlorobenzene.				Benzoyl chloride in CS_2.	
In 200 c.c. flask at 25°.		In 250 c.c. flask at 29·2°.		In 200 c.c. flask at 29·6°.	
R.P.M.	PhCOCl used up.	R.P.M.	PhCOCl used up.	R.P.M.	PhCOCl used up.
122·7	31·99%	124·0	44·19%	132·2	59·39%
126·5	36·34	129·0	51·75	136·6	61·63
132·16	43·61	137·8	59·30	143·3	69·18
143·46	56·10	144·0	62·22	154·8	76·32
151·0	61·91	158·5	65·12	159·0	79·70
162·66	66·00	161·9	63·96	169·2	77·91
169·03	65·40	173·1	62·50	181·0	76·74
175·66	58·69	187·3	61·05		

It will be seen from Table I, that increase in the speed of shaking is not accompanied by a proportionate increase in the amount of benzoyl chloride decomposed. This is probably due to the fact that a violent to-and-fro motion throws the heavier of the two liquids outwards, towards the walls of the flask and prevents an intimate mixing of the two phases. This view is confirmed by the second experiment where the size of the flask is increased. If a solvent of a density higher than monochlorobenzene is used, it is also found that the limiting speed, after which a reduction in the extent of reaction sets in, occurs at a lower value. (Compare Table I).

Variation in the total amount of water.—The solvent used was monochlorobenzene and the experiment carried out in a 250 c.c. flask at 25·8°. Other factors are same as before.

TABLE II.

Amount of water.	Total reaction (N/10-NaOH.)	Reaction per unit vol.	PhCOCl used up.
25 c.c.	47·5 c.c.	1·895	55·1%
50	63·0	1·260	73·1
75	70·9	0·945	82·2
100	73·0	0·730	84·6
125	73·1	0·585	84·9
150	73·5	0·490	85·3

We get here results similar to those obtained in the case of the carbon disulphide-alkali system (*loc. cit.*). As the amount of water increases, the reaction does not increase proportionately but diminishes gradually due to the agitation becoming less vigorous on account of the increase in the volume of the liquid and the decrease in the empty space in the containing vessel.

Variation in the amount of benzoyl chloride solution.—The experiment is performed in two stages. The temperature and the speed of shaking differed in the two stages but were constant for one single stage. The reaction was carried out in flat-bottomed flasks of about 300 c.c. capacity with monochlorobenzene as solvent. The benzoyl chloride solution was 0·4313N. Other factors were the same as in Table I.

TABLE III.

Temp. = 25·2°. R. P. M. = 132 (average).			Temp = 25°·0. R. P. N. = 141 (average).		
PhCOCl soln. added.	Total reaction (N/10-$AgNO_3$).	PhCOCl used up.	PhCOCl soln. added	Total reaction (N/10-$AgNO_3$).	PhCOCl used up.
1·0 c.c.	4·25 c.c.	98·6%	5·0 c.c.	10·25	47·5%
2·0	7·50	87·0	10·0	17·75	41·1
3·0	9·50	73·4	15·0	23·25	35·9
4·0	11·50	60·9	20·0	27·00	31·9
5·0	13·50	60·3	25·0	29·50	27·3
6·0	15·50	60·3			

This system being a perfectly heterogeneous one, the reaction increases proportionately to the amount of benzoyl chloride solution added. When the quantity of benzoyl chloride is very small, it is completely decomposed within the time of the experiment (30 minutes) and hence the slight disproportionality in the initial stages of the reaction.

Effect of the shape of the vessel.—Three flasks with a capacity of about 300 c.c. and of different shapes were selected. Experiments were made with two different speeds with the same flasks. Amounts of reactants, etc., are same as in Table I.

TABLE IV.

Temp. = 25°.

Shape.	R. P. M. = 155. Total reaction (*N*/10-NaOH).	R. P. M. = 47. Total reaction (*N*/10-NaOH).
Conical	55·25 c.c.	62·75 c.c.
Flat bottom	52·5	61·5
Round bottom	48·0	69·0

These results indicate that the conical flask is more efficient in causing a more vigorous agitation of the liquids than the other two shapes. It also appears here that with increase of speed, the difference in the amount of reaction diminishes. But no definite conclusion can be drawn, since we have seen that the reaction does not remain proportional to the speed for all speeds. With higher speeds of shaking, we get a decrease in the extent of the reaction.

Use of Different Solvents.

TABLE V.

Vol. of 0·8626 *N*-benzoyl chloride solution 20 c.c. Amount of water = 50 c.c. Temp. = 24°·8. Time = 30 minutes. Capacity of flask = 250 c.c.

Solvent.	Sp. gravity solvent d_{25}^{25}.	B. p. of solvent at 760 mm.	Total reaction ($N/15AgNO_3$).	PhCOCl decomposed.
CS_2	1·263	46·2°	55·0 c.c.	63·8%
$CHCl_3$	1·480	61·2	35·0	40·6
CCl_4	1·588	76·74	59·0	68·4
C_6H_5Cl	1·1042	132 58	45·0	52·2
C_6H_5Br	1·4886	158·0	37·5	43·5
C_6H_{12}	0·859	138·4	57·5	66·7

The extent of reaction goes on falling in the following order:— Carbon tetrachloride, xylene, carbon disulphide, monochlorobenzene, monobromobenzene, and chloroform, and there is no correlation between the velocity and any single physical property of the solvent.

Velocity Determinations.

TABLE VI.

Amount of H_2O etc., same as in Table I.

Time.	0·8626N-PhCOCl in xylene & H_2O at 25°5 (300 c.c. flask, 106 R.P.M.).	In xylene at 25·°6 (300 c.c flask, 107 R.P.M.).	In $CHCl_3$ & H_2O at 24·8° (250 c.c. flask, 120 R.P.M.).	In CCl_4 & H_2O at 29·4° (138 R P.M.).	In CS_2 & H_2O at 24·8° (114 R.P.M.).	In Ph Br & water at 29° (138 R.P.M.).	In Ph Cl & H_2O at 24·6° (104 R.P.M.).
			0·4313 *N*-PhCOCl				
	K	*K*	*K*	*K*	*K*	*K*	*K*
15	0·0179	0·0178	0·0066	0·0363	0 0158	0·0229	0·0083
30	0·0178	0·0186	0·0075	0·0363	0·0155	0·0235	0·0081
45	0·0179	0·0179	0·0076	0·0352	0·0156	0·0235	0·0082
60	0·0172	0·0179	0·0071	0·0372	0·0163	0·0232	0·0082
75	0·0185	0·0183	0·0070	—	0·0157	0·0226	0·0084
90	0·0181	0·170	0·0074	—	0·0166	0·0215	0·0085

In all these reactions the monomolecular formula is applicable within the limits of experimental error.

This means in other words that the reaction is similar to a homogeneous reaction between two substances, one of which is present in large excess. This is an indirect proof of the complete heterogeneous nature of this reaction.

SUMMARY.

1. The reaction in this system is purely a heterogeneous one, benzoyl chloride being insoluble in water. So, unlike the system, carbon disulphide—alkali, this reaction is very sensitive to agitation. The experiments in agitations in this system give peculiar results, and indicate that, not only does the amount of reaction not increase proportionately to the speed of shaking, but that with higher speed of agitation there is actually a decrease in the amount of benzoyl chloride decomposed. Throwing out of the heavier liquid towards the walls of the vessel appearently causes a diminution of the surface of contact. But by using larger vessels for the reaction we can minimise this influence. The specific gravity of the solvents also clearly shows its own influence, in as much as with heavier solvents a greater decomposition is obtained for the same speeds as compared with lighter solvents.

2. When the volume of water is increased without changing the capacity of the vessel, the extent of decomposition per unit volume is decreased, indicating that the agitation is not so vigorous due to the smaller empty space above the liquids. The fall in reaction per unit volume, here is grater than in the homo-heterogeneous system, because the homogeneous part of the reaction (which is not dependent on shaking) is absent. We have a net increase in the total amount of reaction, since the products of decomposition are removed more rapidly in the larger volume of the solvents available.

3. The reaction increases proportionately to the increase in the quantity of the benzoyl chloride solution.

4. A change in shape of the vessels also markedly influences the reaction, conical flasks being more favourable to the decomposition than flat bottomed or round bottomed ones.

5. When different solvents are used for dissolving the benzoyl chloride, we get different results. The reaction goes on diminishing in the following order:—Carbon tetrachloride, xylene, carbon disulphide, monochlorobenzene, monobromobenzene and chloroform. The effect is not apparently due to any one single physical property of the solvent. The determinations of the velocity of reactions in different solvents go to prove that the monomolecular formula is applicable because one of the reactions (*viz.*, water) is present in excess.

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Effect of Ultraviolet Light on Enzymatic Reactions. Part II. Pepsin.

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The influence of substances like urea, substituted ureas, organic and inorganic ammonium salts on the activity of proteoclastic enzymes, *e.g.*, pepsin, is the subject of investigation in the present paper. As the enzyme pepsin itself liberates amino-acids from protein matters by its action, the influence of the amino-acids like tyrosine, leucine, asparagine, glutamic acid, gelatine, egg-albumin, etc., could not be tried ; their addition would be but to inhibit the direct action of pepsin on proteins. It has been found, as will be evident from the following table of results, that biuret, urea, substituted ureas and ammonium citrate produce a marked increase in the peptic activity of the enzyme. Organic ammonium salts, *viz.*, benzoate, oxalate, tartrate, etc., produce no increment in the activity of the enzyme. An exception, however, is to be found in the case of ammonium citrate which causes a distinct enhancement of the peptic activity. By comparing the results of diastase (*cf.* Banerjee and Sen, *J. Indian Chem. Soc.*, 1935, **12**, 379) with those of pepsin, it is found that ammonium chloride, bromide, formate and benzoate produce no increment in the activities of either of the two enzymes, whereas ammonium citrate causes activation in both the cases. Biuret, urea, substituted ureas, while causing activation of pepsin, fail in the case of diastase. Diamines like *para* or *meta*-phenylenediamine, *m*-toluylenediamine had no effect in the activation of pepsin. It was seen that the diamines unlike the amines were also incapable of decomposing pyruvic acid even at the elevated temperature of 137° (*cf.* Banerjee and Sen, *Trans. Nat. Inst. Sci. India*, 1935, **1**, 83). Attempts were also made to enhance the peptic activity further by treatment with ultraviolet light together with the so-called catalysts. Unlike diastase, (Banerjee and Sen, *loc. cit.*) the ultraviolet rays could not affect the activity of pepsin at the particular hydrogen-ion concentration of the substrate considered. The protein substrate itself might protect the enzyme from the destructive action of the ultraviolet rays, just as it will be remembered that the destruction of the diastatic activity by ultraviolet light (*cf.* Pincussen, *Biochem. Z.*, 1923, **134**, 459;

1924, **144**, 366; 1924, **152**, 406) is considerably arrested by the addition of small quantities of protein matters, *e. g.*, albumin, gelatin, etc. (Banerjee and Sen, *loc. cit.*). The matter has been fully discussed previously. In the human system perhaps this protein matter protects the tissues from the injurious effect of the ultraviolet rays, for it is known that the rays cannot penetrate much below the epidermis of the human system.

As in the case of diastase, four sets of experiments were carried out in the case of pepsin also *viz.*, (*i*) without accelerator, (*ii*) with accelerator, (*iii*) with accelerator and ultraviolet light and (*iv*) without accelerator and with ultraviolet light.

Experimental.

Measurement of the peptic activity.—The measurement of the activity of the enzyme presented much technical difficulty at the outset. Sorensen's method of formol titration of the liberated amino-acids though conveniently applicable in the case of trypsin or Willstätter's method of thymolphthalein titration (*Ber.*, 1921, **54**, 2988; *cf.* also Harris, *Proc. Roy. Soc.*, 1923-24, **B**, **95**, 500) was found not to be satisfactory in the present system of experiments. The measurements of the peptic activity were made by the comparative method of Gross (*Arch. Exp. Path. Pharmakol.*, 1906, **58**, 157) who suggests a solution of very pure caseinogen as the protein substrate for the enzyme. The substrate is prepared by dissolving 1 g. of pure caseinogen in 16 c. c. of 25 % HCl (*d* 1·124) in a 1000 c.c. flask on a water-bath and diluting to 1000 c.c. The undigested caseinogen can be precipitated by a 20% solution of sodium acetate.

Preparation of pure caseinogen.—1000 C.c. of skimmed milk were diluted six times with water and the caseinogen precipitated by adding with constant stirring, about a litre of dilute acetic acid (10 to 15 c.c. of glacial acetic acid in 1000 c. c. of water), avoiding excess of the latter. The precipitate was allowed to settle and the solution decanted ; the former was washed with large volume of distilled water, till free from acid. The precipitate was then dissolved in dilute ammonia to form a solution neutral to litmus. It was diluted with a large volume of water and the caseinogen reprecipitated with dilute acetic acid, avoiding excess of the latter. The precipitate was washed free from acid, redissolved in ammonia and reprecipitated with acid. The operation was repeated several times. The precipitate was finally filtered and

washed free from acid. It was then suspended in about 1000 c.c. of $N/10$-HCl and churned for about 2 hours to remove the inorganic salts. The process was repeated. The precipitate was finally washed free from acid and treated several times with large volumes of alcohol and ether and dried at room temperature. It was finally ground and dried at 40-45°.

Procedure.—In each of a series of ten clean and numbered test tubes of approximately the same bore, are placed 10 c.c. of the acid caseinogen solution. The p_H of the caseinogen substrate was generally maintained at 1·8, the optimum for the pepsin reaction. The tubes with their contents were warmed to 40° in a constant temperature bath. To each of the tubes then a progreesively increasing amount of the enzyme solution, *i.e.*, 0·1 c.c. in the first tube, 0·2 c.c. in the second, and so on, was added as quickly as possible. The series of test tubes was replaced in the bath and kept for half an hour. The tubes were then taken out and 1 c.c. of 20% sodium acetate solution was added very quickly to each tube; the undigested casein was precipitated. The smallest quantity of the enzyme required to digest the 10 c.c. of the caseinogen solution at the given time, is the value noted, *i.e.*, the first clear tube of the series is taken as the index. The turbidity and clarity of the contents of the tubes were finally checked by the nephelometer. If 1 c. c. of the pepsin solution be the basis of calculation and 0·025 c. c. was sufficient, then the pepsin solution corres ponds to $1/0{\cdot}025 = 40$ units. The enzyme solution used was generally a 2 % solution of pepsin.

As in the experiments with diastase (Banerjee and Sen, *loc. cit.*), the p_H of the caseinogen substrate for pepsin was checked with and without the accelerators and always kept constant for the same set of experiments. This was necessary to show that the effect of the activators is not due to a more favourable hydrogen-ion concentration induced by their presence. That the action of the so-called activators is also not due to the deviation of the iso-electric point of precipitation of caseinogen induced by their presence, is evident from the fact that the p_H of the content of the tube taken as index, after the addition of the sodium acetate solution, was very near the iso-electric point of precipitation of caseinogen. Even the addition of very small amounts of $N/100$-alkali to the 'index' tube did not make any precipitate appear, thus deviating the resulting p_H value more towards the iso-electric point of precipitation of caseinogen which is 4·7.

The experiments with ultraviolet light were carried out in quartz tubes and in an incubator adjusted at 40°. The exposure was generally for 15 minutes at a distance of two feet with a mercury-vapour lamp of 3000 C. P. and 12″ arc. Further work with other proteoclastic enzymes, *e.g.*, papain, trypsin, etc., is in progress. The results are tabulated below.

TABLE I.

1 C. c. of 0·1 % soln. used. p_H of the substrate = 1·8.

Substance.	Control expt. Peptic value P_1.	With catalyst Peptic value P_2.	With catalyst and ultraviolet. Peptic value P_3.	Control expt. without catalyst with ultraviolet. Peptic value P_4.	pH of the 1st clear tube, after addition of Na-acetate soln.
Urea	2 units	2·5 units	2·5 units	2·0 units	4·4
Biuret	2·0	3·3	3·3	2·0	4·4
* Phenylurea	1·43	2·0	2·0	1·43	4·3
Thiourea	1·66	2·0	2·0	1·66	4·4
Phenylthiourea	2·0	2·5	2·5	2·0	4·4
Allylthiourea	2·0	2·5	2·5	2·0	4·4
Ammon. citrate	2·0	2·5	2·5	,,	4·4
Ammon. oxalate	2·0	2·0	2·0	,,	4·3
Ammon. benzoate	,,	,,	,,	,,	4·3
Ammon. tartrate	,,	,,	,,	,,	4·4
Ammon. bromide	,,	,,	,,	,,	4·3
Ammon. iodide	,,	,,	,,	,,	4·3
Ammon. chloride	,,	,,	,,	,,	4·4
p-Phenylenediamine	,,	,,	,,	,,	4·4
m-Toluylenediamine	,,	,,	,,	,,	4·4

* pH of the substrate in this case is 1·9.

DISCUSSION.

The idea that the enzyme is composed of a portion which is specifically catalytic and another portion which is essentially a colloidal substance, has been more or less established, from previous work. In

fact, the purification of an enzyme consists in eliminating unnecessary accompanying matters, leaving these two portions intact. The colloidal portion, however, may suffer greater and greater degree of dispersion (*cf.* Pincussen and co-workers, *Biochem. Z.*, 1924, **144**, 366; 1926, **171**, 1; 1928, **195**, 79; also Banerjee and Sen, *loc. cit.*) whilst the catalytic portion remains as before. This increased dispersion may no doubt be expected to increase the catalytic activity owing to the greater surface caused by dispersion, but at the same time it may also be conjectured that this increased dispersion produces susceptibility to easy de-activation. The influence of ions on the coagulation or "coarsening" of the colloid particles, has been held to be the reason for this de-activation. Pincussen and his school (*loc. cit.*) have laid special stress on this aspect. In their work on the influence of ultraviolet light on the activity of pepsin (*cf.* Pincussen and Kekusji Uehara, *Biochem. Z.*, 1928, **195**, 87) they have shown that the effect of a potassium ion is more de-activating than that of calcium ion. This characteristic, however, is not throughout maintained. In another series of experiments, they have shown that the action of ultraviolet light on the hydrolysis of fibrin by pepsin is negligible if the p_H value lies between 1·93 and 2·28. Between the p_H values 1·15 and 1·42, the de-activation of the enzyme appears to be distinct and prominent. In other words, with stronger acidity, the difference between the hydrolytic capacities in ultraviolet and in the absence of ultraviolet, is very much noticeable. Specially, working at p_H 1·15—1·19 according to the present method, however, no such action of ultraviolet light as reported by Pincussen was noticed by us.

It is a question that should be asked here, what is the optimum p_H value for the hydrolysis of fibrin on one hand, and other types of proteins on the other by pepsin. Thus for caseinogen the optimal p_H value for the hydrolytic action of pepsin, has been laid down to be 1·8 (Northrop, *J. Gen. Physiol.*, 1919, **1**, 607; 1920, **3**, 211; 1922, **5**, 263), whereas from Pincussen's experiments with ox-fibrin or sheep-fibrin, 1·15-1·17 appears to be the optimum; in the experiments of the present paper (where the method of determining the hydrolytic activity of pepsin is different) at the optimum p_H of 1·8, there does not appear to be any difference in the hydrolysis of caseinogen whether under the influence of ultraviolet or without it. It is in this region of p_H value that Pincussen and his collaborators also find no influence of ultraviolet light on the activity of pepsin on fibrin.

One must notice here that the values of the hydrolytic dicomposition of the proteid matter by pepsin may be different according to the method of determination of the peptic value.

In Sorensen's work (*Biochem. Z.*, 1909, **21**, 131), it has been shown that the optimal action of pepsin, measured in the digestion of egg-albumin, corresponds to a strongly acid reaction, the optimal p_H being about 1·5, if the duration of the experiment is short; upon more prolonged or extensive transformation, however, there is noticed a considerable expansion in the region of optimal activity in the direction of lower acidity. The cause of this change has not yet been recognised. According to Northrop (*loc. cit.*) the dependence of the action of pepsin is influenced, like that of other proteolytic enzymes, by the ionisation state of the substrates used. According to this view, the action of pepsin is to be attributed to its reaction with protein cations. Its p_H optimum is then displaced at the same time as the iso-electric point of the substrate. The optimum p_H for the hydrolysis of caseinogen by pepsin has been found to be 1·8 and that for hæmoglobin and gelatine 2·2. The results obtained in the present investigations for the optimum p_H dependence of pepsin for the hydrolysis of casein, are given in Table II. The nature of the reactions is such that if activity—p_H, curve is drawn it will be found that with the increase of p_H, peptic value rises till it reaches a maximum and then it tends to decrease.

TABLE II.

p_H values	...	1·4	1·6	1·8	2·0	2·2
Peptic values	...	1·66	1·818	2·00	1·75	1·43

One notices the fundamental difference that whilst Pincussen and others had fibrin in an undissolved state for the pepsin to act upon, in the present case caseinogen was obtained in an optically clear solution for the enzyme to work upon. This no doubt would ensure a greater homogeneity in the hydrolytic decomposition of the protein, and in fact, place the analytical data on a better foundation. The uncertainties of the soluble amino-acid adsorption on the undissolved fibrin to which Pincussen refers in his work, have thus no influence in the method of determination followed in the present case. To explain the so-called de-activating influence of ultraviolet light at lower p_H concentrations (*cf.* Pincussen and Uehara, *loc. cit.*), one must look for an explanation which is dependent on the ionic activity

under the influence of ultraviolet light (*vide supra*). At higher hydrogen-ion concentration, probably the colloidal particles of the enzyme-complex which are already sensitive to the action of ultraviolet light are transformed into bigger particles, thus rendering the enzyme-complex less active. That at a slightly higher p_H value (1·8) there is no de-activation, may be due to the dimension of the colloidal particles themselves. In other words between p_H 1·15 and 1·42, the degree of dispersion of the colloid particles is probably such that they are in that state most affected by light percussions. Whether one could not correlate the dimensions of the particles of the enzyme-complex at this stage of dispersion and the wave-lengths of the lights, is a matter for consideration. An alternative idea to explain the non-de-activation at p_H 1·8 may be found in the assumption, that at that hydrogen-ion concentration, the enzyme-complex forms a further complex with the acid or its ions, which is not sensitive to the action of ultraviolet light. The exploration of the catalytic activities of the enzyme both below and above the optimal p_H regions under the influence of ultraviolet light would be of great importance in understanding the nature of the enzyme-complex itself. It seems clear, however, from the present work that the general characteristic of proteins to act as a protector against the ultraviolet rays in the case of diastase (*loc. cit.*) is maintained here also.

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Condensation of Succinic Anhydride with Phenols and Phenolic Ethers. Synthesis of Derivatives of Tetrahydronaphthalene. (Preliminary Note).

By P. C. Mitter and Shyamakanta De.

Rosenmund and Schapiro (*Arch. Pharm.* 1934, **272**, 313) have found that anisole condenses with succinic anhydride in presence of aluminium chloride in nitrobenzene medium to give γ-*p*-methoxyphenyl-γ-ketobutyric acid. We have found that the reaction proceeds smoothly in acetylene tetrachloride medium at ordinary temperature with almost theoretical yield. The ketonic acid gives a semicarbazone, m.p. 185-86° (decomp.).

Reduction by Clemmensen's method gives γ-*p*-methoxyphenylbutyric acid, m.p. 60°. Dehydration of this substance with phosphorus pentoxide in benzene medium, gives 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 61°. It gives a semicarbazone, m.p. 221°. Further Clemmensen reduction gives 1:2:3:4-tetrahydronaphthol-7-methyl ether, m.p. 146°.

Veratrole, under similar conditions, gives rise to γ-3 :4-dimethoxyphenyl γ-ketobutyric acid, m.p. 163°. Its semicarbazone melts at 177°. Clemmensen reduction gives γ-3:4-dimethoxyphenylbutyric acid, m.p. 61°. Dehydration with phosphorus pentoxide gives 1-keto-6 : 7 (or 7 : 8)-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 99°-100°. The semicarbazone melts at 242-43°.

Phenol condenses with succinic anhydride under similar conditions giving rise to γ-*o*-hydroxyphenyl-γ-ketobutyric acid*, m.p. 146°. identical with the acid prepared by Rosenmund and Schapiro (*loc. cit.*) from 2-oxy-β-chlorpropionylbenzol of Meyer and Zutphen (*Ber.* 1924, **57**, 200) over the nitrile. Clemmensen reduction gives γ-*o*-hydroxyphenylbutyric acid, m.p. 65-66°. The work is being extended.

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* This substance has been prepared by an identical method by Nargund and Rawal (*Private communication*).

Methyl Red as an Adsorption Indicator (A Note).

By Dhirendra Mohan Mukherjee.

The mechanism of the adsorption of dyestuffs, specially of indicators by polar precipitates is of interest in relation to the use of 'adsorption indicators' in volumetric titrations. Quantitative estimations of the amount of indicators adsorbed by silver halides under different conditions of precipitations are being carried out in this laboratory with measurements of consequential changes in p_H values and specific conductivities. It is expected that these experiments would throw light on the mechanism of the adsorption of indicators by polar precipitates. The results (mean of two parallel experiments) given below indicate that

(*a*) the p_H is mostly on the acid side in agreement with previous observations of Basu in this laboratory that precipitation of silver halides by double decomposition from the pure neutral salts produces an acid reaction;

(*b*) that the manner of precipitation from the same amounts of the reactants affects the adsorption of the indicator and

(*c*) that the adsorption of the indicator probably affects to some extent the p_H of the final system.

Absorbent—AgCl (4×10^{-3} g. mol.). Adsorbate—Methyl red.
Time = 1 hr.

Condition of expt. (0·1*N* soln. used).	Indicator adsorbed $\times 10^4$.	With methyl red. p_H.	With methyl red. Sp. conducty. $\times 10^4$ at 35°.	Without methyl red. p_H.	Without methyl red. Sp. conducty. $\times 10^4$ at 35°.
I. Equivalent amount.					
$AgNO_3$ added to KCl.	0·31 g.	5·50	61·34	5·47	62·27
KCl ,, $AgNO_3$	0·73	5·55	60·42	5·60	61·97

Condition of expt.	Indicator abrorbed $\times 10^4$.	p_H.	Sp. conducty. $\times 10^4$ at 35°.	p_H.	Sp. conducty. $\times 10^4$ at 35°.
II. KCl in excess (5×10^{-5}g. mol.).		With methyl red.		Without methyl red.	
$AgNO_3$ added to KCl	0·58	5·72	59·84	6·40	63·45
KCl ,, $AgNO_3$	0·71	5·58	62·87	5·34	63·39
III. $AgNO_3$ in excess (5×10^{-5} g.mol.).					
$AgNO_3$ added to KCl	0·70	5·54	61·19	5·60	62·21
KCl ,, $AgNO_3$	2·1	5·52	61·66	5·82	62·42

The method used in determining the p_H and the adsorption of the indicator will be described when the results are published in full.

The author's thanks are due to Professor J. N. Mukherjee for permission to work in his laboratories and for other facilities and to Mr. N. P. Chatterjee for helpful criticisms.

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Review

Candle Manufacture (with special reference to tropical countries), By Dr. N. N. Godbole, Benares Hindu University, pp. 29. Price Rs. 2 (foreign 4 sh.)

Solid glycerides like tallow were formerly used in candle making ; these gave place to solid esters like Beeswax. But from the point of view of use in tropical countries both were found to be defective. With the advent of paraffin candles and with the discovery that stearic acid could be nicely blended with paraffin to have the desired melting point, candle manufacture became a practicable one. These points are given in detail in "Candle manufacture" by Prof. N. N. Godbole of the Benares Hindu University. The chapters on splitting of oils, impregnation of wick and the blending of stearic acid and other substances with paraffin are really instructive. Judging from the historical survey and the details with illustrations, of the various stages of the manufacture of candle, the book can be safely recommended for our students of applied chemistry.

M. N. G.

Chemical Examination of the roots of Rauwolfia Serpentina and Studies in the alkaloids of Holarrhena Antidysenterica By R. H. Siddiqui.

This booklet is the reprint of a thesis submitted for the degree of Doctor of Philosophy of the University of Aligarh. The author has isolated five alkaloids from *Rauwolfia Serpentina* and characterised the alkaloids by the preparation of certain derivatives. The constitution and relationship of these alkaloids have not yet been cleared up.

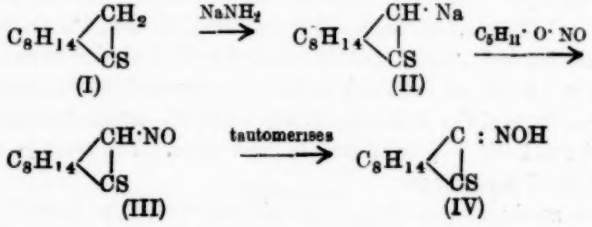
The author has also studied the action of cyanogen bromide on conessine, and shown how *iso*conessimine and conimine (two subsidiary alkaloids of *Holarrhena Antidysenterica*) could be obtained from conessine, thus confirming the ideas of S. Siddiqui on the close relationship between these three alkaloids. The thesis should be of interest to workers in the field of plant chemistry.

S. N. C.

Studies in the Camphor Series. Part II. Synthesis of *iso*Nitrosothiocamphor and its Application as an Indicator in Acidimetry and Alkalimetry.

By Dines Chandra Sen.

According to the structure ascribed to thiocamphor in a recent communication by the author (*J. Indian Chem. Soc.*, 1935, **12**, 647), it was expected that the substance would yield an *iso*nitroso derivative like camphor. The preparation of this compound has been possible by the interaction of *iso*amyl nitrite on thiocamphor in presence of sodamide. The corresponding camphor derivative has been prepared by a similar method using powdered sodium ethoxide in place of sodamide (Forster, *J. Chem. Soc.*, 1905, **87**, 232; Claisen and Manasse, *Ber.*, 1889, **22**, 530). The formation of *iso*nitroso derivative can be represented by the following scheme:



The above synthesis leads to the constitution of *iso*nitrosothiocamphor as described in Formula (III). The tautomeric change from (III) to (IV) is supported from its properties.

The substance forms a red sodium salt and is soluble in caustic alkalis forming a red solution which when acidified gives violet crystals. The alkaline solution when diluted changes from red to yellow. It is sparingly soluble in water and dilute mineral acids but soluble in common organic solvents like alcohol, ether, benzene, acetic acid etc. giving violet solutions. A very dilute solution in aqueous alkali practically seems to be colourless or very faintly coloured (violet). The colour change in acids and alkalis is very sensitive and it was, therefore, thought that the compound might be useful as an indicator.

Besides its capacity to form a sodium salt as described above, it also forms a benzoyl derivative and organic complexes with chlorides of cobalt, nickel, etc. with evolution of hydrochloric acid. The detailed description of these derivatives will be the subject of a future communication. All these reactions, however, show that the substance contains an easily replaceable hydrogen atom, for which it is slightly acidic in behaviour, and this hydrogen must be the one attached to the N·OH group. The substance should, therefore, be represented as in (IV). The formation of an *iso*nitroso derivative is characteristic of substances containing $-CH_2-CO-$ group. It is now found that this reaction is characteristic also of substances containing $-CH_2-CS-$ group, and that thiocarbonyl group imparts similar reactive nature to an adjacent methylene group. As previously described, a very dilute solution of the substance in acid solution is practically colourless and in alkaline solution it is yellow. Though the transformation of colour actually takes place from violet to yellow yet under the conditions of the experiment the substance may be considered as an unicoloured indicator. The transition range lies between p_H 8·6 and 9; p_K being 8·8. The above p_H values were obtained by adding equal amounts of the indicator of varying concentrations to equal volumes of Clark and Lub's standard buffer solutions. For example 0·5 c.c. of 0·04% solution in 60% alcohol, 1·2 c.c. of the same solution and 0·5 c.c. of 0·5% solution in 70% alcohol were added in each case to 10 c.c. of Clark and Lub's standard buffer solutions. Larger volumes of the indicator (0·5% solution) cannot be added, as the indicator itself is precipitated in that case. The same p_H range was obtained in each case.

From an observation of the range of transformation of some of the more useful indicators, such as methyl orange, methyl red, phenolphthalein, bromophenol blue, bromothymol blue, thymol blue, etc. it is interesting to note that the p_H ranges vary from 1·3 to 2·1, whereas in the case of *iso*nitrosothiocamphor it is only 0·4. Special interest attaches to this indicator in view of its being (*i*) a thioketone, (*ii*) a nitroso derivative, none of which has previously responded to such colour changes and (*iii*) its availability for use for titration of weak organic acids. A phenolic acid (salicylic acid) has also given satisfactory results with sodium hydroxide and barium hydroxide solutions with this indicator. One of the defects of this indicator, however, is that it cannot be used in cold for the titration of sodium carbonate solutions. But if the solution to be titrated is boiled for 3-4 minutes

after adding nearly the required amount of carbonate to a known volume of acid, and the titration be completed by adding carbonate into the hot solution drop by drop, the sharp end-point is easily obtained. In this case large excess of dissolved carbon dioxide affects the reagent to a certain degree.

The colour change of the indicator may be attributed to a difference in ionisation of the reagent in the free state and of its sodium salt as shown below:

The stock solution to be used as the indicator consists of a 5% solution of *iso*nitrosothiocamphor in a 70% solution of alcohol, one or two drops of which are necessary for each titration. With this indicator it has been possible to estimate the strength of alkalis like NaOH and $Ba(OH)_2$ solutions, strong acids like hydrochloric acid and sulphuric acid, and weak organic acids like acetic, oxalic, succinic, and salicylic acids etc. The organic acids give the same result both in aqueous and alcoholic solutions. Though the results of titration are found to be identical in the case of both phenolphthalein and *iso*nitrosothiocamphor, yet from the short p_H range of the latter, it is apparent that the results of titration with the new indicator should be much more accurate than those with phenolphthalein.

Experimental.

A solution of thiocamphor (17 g.) in ether (15 c.c.) was mixed with *iso*amyl nitrite (12 g.) and the solution was well cooled (0°) for half an hour. Sodamide (4 g.) suspended in sodium-dried ether (7 c.c.) was taken in a long necked flask (250 c.c.) fitted with a calcium chloride guard-tube and was similarly cooled to 0° for nearly 15 minutes. The solution of thiocamphor in *iso*amyl nitrite was slowly poured little by little over sodamide. The vigorous reaction was controlled by careful slow mixing of the materials and continued stirring. The red solution of thiocamphor slowly changed to dark red. The mixture was then kept at a very low temperature for another half hour, after which it was mixed with ice-cold water and shaken with ether to remove unchanged *iso*amyl nitrite and thiocamphor. The aqueous solution was then treated with dilute acetic acid

whereby violet crystals of *iso*nitrosothiocamphor separated out. The crystals were separated by filtration, washed with water, and crystallised from alcohol or ether, m.p. 148°. The needle-shaped crystals when precipitated from alcoholic solution by means of water appear grey and when crystallised from hot concentrated solutions appear bluish violet. It is soluble in acetic acid (both strong or dilute) giving a violet solution and with aqueous alkalis it produces a red solution which changes to yellow on dilution. The substance, however, is practically insoluble in dilute mineral acids. The compound gives a red coloured precipitate with cobalt salts, a reaction which is very characteristic for the detection of cobalt. It is very sensitive and can detect cobalt up to an extent of 1 part of cobalt per 50,000 parts of water. With nickel salts it gives a greenish brown precipitate. The precipitate with cobalt is insoluble in water and dilute acetic acid, whereas that with nickel is soluble in dilute acetic acid. Experiments, now in progress, suggest that the substance is a suitable reagent for the quantitative estimation of cobalt. (Found: C, 60·62,; H, 7·69; N, 7·08; S, 16·09. $C_{10}H_{15}ONS$ requires C, 60·91; H, 7·61; N, 7·11; S, 16·24 per cent).

The following data give an idea of the usefulness of the reagent as an indicator in acidimetry and alkalimetry.

TABLE I.

Strong acids.

Reagents.	Conc.	Alkali required for 10 c.c. acid with: Methyl orange.	Methyl red and methylene blue (mixed indicator.)	Phenolphthalein.	*iso*Nitrosothiocamphor.
H_2SO_4, Na_2CO_3	1*N*	10 c.c.	10 c.c.	...	9·95 c.c.
H_2SO_4, NaOH	0·1	10	10	10·05 c.c.	10·05
,, ,,	0·05	10	10	10·05	10·05
,, ,,	0·025	10	10	10·05	10·05
,, ,,	0·02	10·05	10·05	10·1	10·1
HCl, $Ba(OH)_2$	0·1	9·95	...	10	10
,, ,,	0·05	9·95	...	10	10

TABLE II.

Weak acids.

Reagents.	Conc.	Alkali required for 10 c.c. acid with Phenolphthalein.	Alkali required for 10 c.c. acid with *iso*Nitrosothiocamphor.
Oxalic acid, NaOH	0·1*N*	9·95 c.c.	9·95 c.c.
,, ,,	0·05	9·95	9·25
,, ,,	0·025	10	10
Succinic acid, NaOH	0·1	9·95	9·95
Succinic acid, $Ba(OH)_2$	0·1	10	10
,, ,,	0·05	10	10
Salicylic acid, NaOH	0·1	9·95	9·95
,, ,,	0·05	9·95	9·95

The above results show that in the titration of a strong acid with a strong alkali the reagent is equally suitable like the more common indicators. At higher dilutions of the acids and alkalis the results are, as is to be expected, slightly affected, the order of deviations, nevertheless, being the same in the case of all the indicators. With weak acids (the standard solutions of which have been prepared by direct weighing), the reagent is quite as good an indicator as phenolphthalein, though owing to hydrolytic effects the apparent neutralisation points correspond with a lower value of the alkali than in the case of the stronger acids.

SUMMARY.

1. *iso*Nitrosothiocamphor has been synthesised by the action of *iso*amyl nitrite on thiocamphor in presence of sodamide and its constitution has been established.

2. The usefulness of this substance as an indicator has been proved in the case of both strong and weak acids. The p_H range is rather narrow: p_H 8·6 to 9; $p_k = 8·8$.

3. The substance has also been used as a sensitive reagent for the detection of cobalt ; sensitiveness being 1:50,000.

In conclusion, I desire to express my sincere thanks to Sir P. C. Rây to whom I am indebted for the research facilities in his laboratory. My thanks are also due to Mr. A. S. Bhattacharjee and Mr. R. Mitra of the Physical Chemistry laboratory for kindly helping me in taking a few observations in connection with the determination of sensitiveness of the reagent as an indicator.

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Denitrification in Sunlight and its Retardation. Part II.

By N. R. Dhar and S. K. Mukherji.

In a recent communication (*J. Indian Chem. Soc.*, 1935, **12**, 67) it has been shown that nitrogen *in the gaseous state* is lost from soils when the conditions are favourable for oxidation on exposure to light and air.

We have observed that the loss of nitrogen on exposing ammonium salt solutions to air is always greater in light than in the dark. Solutions of ammonium chloride and sodium nitrite have been found to decompose readily with evolution of nitrogen gas when exposed to sunlight mixed with sterilised and unsterilised soils. This decomposition is considerably less in dilute solutions containing ammonium and nitrite ions and when the temperature is low. Cane-sugar has been found to be a retarder of this type of denitrification.

All these and other observations on the nitrogen loss from soils under aerobic conditions have been explained from the view point that in the processes of ammonification and nitrification taking place in the soil or in solution, ammonium nitrite is produced, which decomposes readily into nitrogen and water by increase of temperature or exposure to light. The formation of ammonium nitrite from ammonium salts or proteins requires oxygen and that is why, this type of denitrification is facilitated by increased soil aeration and also soil acidity, as nitrous acid undergoes decomposition according to the equation,

$$3\,HNO_2 \rightleftharpoons HNO_3 + 2\,NO + H_2O.$$

Addition of carbonaceous substances like molasses tends to preserve the soil nitrogen by decreasing the velocity of the oxidation of the nitrogeneous compounds present in the soil and thus decreasing the probability of the formation and decomposition of ammonium nitrite.

This type of denitrification observed when the soil conditions are favourable for oxidation, first studied by Lipman and Blair (*Soil Sci.*, 1921, **12**, 1) and emphasised by Russel ("Soil Conditions and Plant Growth," 1932, pp. 367-69) has now been satisfactorily explained by Dhar and collaborators (*Nature*, 1934, **134**, 572; *J. Indian Chem. Soc.*, 1935, **12**, 67). As this phenomenon is of very great importance specially under tropical conditions, we are continuing our researches on this

type of nitrogen loss, which may be greater in amount than the nitrogen required by a crop growing on the soil.

Our experimental results recorded in this paper can be divided into four parts, *viz.*, (1) decomposition of solutions of ammonium nitrite when exposed to artificial light, (2) nitrogen loss from mixtures of ammonium chloride and potassium nitrite when mixed with powdered soil and exposed to sunlight in the summer months, (3) loss of nitrogen when α-alanine and potassium nitrite are mixed with soil and exposed to sunlight, (4) loss of nitrogen in the gaseous state by exposing ammonium salts and nitrites in quartz vessels under sterile conditions.

Decomposition of Solutions of Ammonium Nitrite.

A solution of barium nitrite was mixed with an equivalent amount of solution of ammonium sulphate in a quartz cell and the barium sulphate allowed to settle and the solution exposed to the total light from a gas-filled tungsten filament lamp of 1000 watt. A parallel beam of light was obtained by a quartz lens. In order to keep the temperature of the solution in the quartz cell constant, a steady current of water from a thermostat was circulated. The results obtained are given in Table I.

TABLE I.

NH_3-N added as $(NH_4)_2SO_4$ = 0·14 g. NO_2-N added as $Ba(NO_3)_2$ = 0·159 g. Total N added (Devarda's) = 0·2999 g.

Treatment.	NH_3-N left.	NO_2-N left.	Total N left.	NH_3-N lost.	NO_2-N lost.	Total N lost.	% Lost.
Exposure at			*Light*				
40° for 5 hrs.	0·133 g.	0·151 g.	02859 g.	0·007 g.	0·008 g.	0·014 g.	4·5
40° for 10 hrs.	0·1228	0·1414	0·2646	0·0172	0·0176	0·0353	11·7
40° for 20 hrs.	0·1038	0·1206	0·2235	0·0382	0·0384	0·0764	25·4
50° for 5 hrs.	0·1295	0·1480	0·2789	0·0105	0·011	0·021	7
50° for 10 hrs.	0·112	0 1290	0·2438	0·028	0·03	0·056	18·6
50° for 20 hrs.	0·083	0·100	0·1859	0·057	0·059	0·114	38·1
Kept at			*Dark*				
40° for 5 hrs	0·1388	0·1572	0·2974	0·0012	0·0018	0·0025	0·8
40° for 10 hrs.	0·1330	0·151	0·2859	0·007	0·008	0·014	4·6
40° for 20 hrs.	0·1225	0·141	0·2649	0·0175	0·018	0·035	11
50° for 5 hrs.	0·1352	0·154	0·2902	0·0048	0·005	0·0097	3·2
50° for 10 hrs.	0·1256	0 1446	0·2711	0·0144	0·0144	0·0288	9·6
50° for 20 hrs.	0·104	0·125	0·2279	0·036	0·034	0·072	24

The experimental results show that the rate of decomposition of solutions of ammonium nitrite both in light and in the dark are autocatalytic. The velocity goes on increasing as the chemical change progresses. The p_H of the solutions were also estimated before and after decomposition and no change was observed.

Many years ago Arndt (*Z. physikal. Chem.*, 1901, **39**, 64) showed that the thermal decomposition of ammonium nitrite is accelerated by acids and retarded by ammonia. A very interesting point is brought out by our researches that the ratio of the photochemical and thermal decomposition of ammonium nitrite solutions at 40° is higher than the same ratio obtained at 50°. In other words, when the temperature is high, the thermal decomposition of ammonium nitrite becomes quite prominent.

TABLE II.

Treatment. After	Loss of nitrogen Dark and light.	Dark only.	Light only.	Percentage loss in Dark.	Light.
5 hrs. at 40°	0·014 g.	0·0025 g.	0·0115 g.	0·8	3·8
10 hrs. at 40°	0·0353	0·014	0·0213	4·6	7·1
20 hrs. at 40°	0·0764	0·035	0·0414	11·0	13·9
5 hrs. at 50°	0·021	0·0097	0·0113	3·2	3·8
10 hrs. at 50°	0·056	0·0288	0·0272	9·6	9
20 hrs. at 50°	0·114	0·072	0·042	24	14

Decomposition of Mixtures of Ammonium Sulphate and Potassium Nitrite Mixed with Dry Soil.

Powdered unsterilsed garden soil was mixed with different amounts of ammonium sulphate and potassium nitrite in enamelled shallow dishes and covered with glass plates and exposed to sunlight daily for 9 hours from 9th March till 13th July 1935. No water was added in these experiments In order to obtain comparable results in the dark, in one set of experiments the glass covers were blackened on the outside with a thick coating of Japan black enamel to cut off light and the dishes with blackened glass covers were also put in the sun in order to obtain the thermal decompositions under identical conditions. The results obtained are recorded in Table III.

TABLE III.

NH_3-N added.	NO_2-N added.	Total N added.	NH_3-N left.	NO_2-N left.	NO_2-N formed.	Total N left.	Total N loss.	% Loss.
				Light				
0·5%	0·0%	0·5%	0·1609	0·0020	0·02	0·182	0·318	63·6
0·0	0·5	0·5	0·0021	0·14	0·2699	0·42	0·088	17·6
0·25	0·25	0·5	0·0312	0·14	0·021	0·192	0·308	60·1
0·4	0·1	0·5	0·0875	0·00934	0·0912	0·1881	0·3119	62·3
0·1	0·4	0·5	0·0107	0·168	0·0887	0·25	0·25	50
0·3	0·2	0·5	0·04	0·084	0·0635	0·1875	0·3125	62·5
0·2	0·3	0·5	0·018	0·0934	0·0586	0·17	0·33	66
				Dark				
0·5	0·0	0·5	0·35	0·0002	0·0395	0·3897	0·1103	22
0·0	0·5	0·5	0·002	0·3759	0·0665	0·4444	0·0556	11
0·25	0·25	0·5	0·39	0·2012	0·0092	0·2942	0·2502	50
0·3	0·2	0·5	0·078	0·1258	0·026	0·2298	0·2752	55
0·2	0·3	0·5	0·0268	0·1489	0·035	0·2092	0·2908	58

The experimental results show that in the heat of summer months there is considerable thermal decomposition of ammonium nitrite, but the decomposition in sunlight is appreciably greater than in the dark. In Allahabad in months of April, May and June the temperature in the sun goes up to 75° and hence the ammonium salts, specially the nitrite, undergo codsiderable decomposition even when mixed with ordinary powdered soil containing only 5·6 % moisture. Ammonium sulphate also undergoes considerable loss. The potassium nitrite when mixed with dry soil is oxidised to nitrate to a large extent and undergoes a slight loss of nitrogen probably due to the decomposition of nitrous acid formed by the action of carbonic acid on the potassium nitrite.

Nitrogen Loss from Mixtures of α-Alanine and Potassium Nitrite Mixed with Soil.

Another set of experiments was carried on by mixing α-alanine and potassium nitrite with ordinary soil and exposed to sunlight in

open beakers from 19th February to 7th March, 1935. The results in Table IV show that there is considerable loss of nitrogen even in these experiments.

TABLE IV.

Amino acid N added.	NO_3-N added.	Total N originally present.	NH_3-N left.	NO_3-N left.	NO_3-N formed.	Total N added.	Total N left Kjeldal.	% N Loss.
Exposure to sunlight = 114 hours.								
0·0906%	0·1015%	0·035%	0·0204	Traces	0·00169	0·2271	0·0875	61·4
0·0906	0·203	0·035	0·1868	0·0823	0·00169	0·3296	0·0667	72·1
0·1812	0·203	0·035	0·0114	0·1270	0·08	0·35	0·1000	35·1
0·1812	0·1015	0·035	0·0175	0·0005	0·00129	0·3177	0·0778	75·3
0·0906	0·000	0·035	0·0208	0·0005	0·000	0·1256	0·1008	1·1
0·1812	0·000	0·035	0·036	0·0012	0·00164	0·2162	0·175	1·8
0·000	0·1015	0·035	0·0009	0·056	0·0454	0·1365	0·04	22·3
0·000	0·203	0·035	0·0007	0·1167	0·0862	0·238	0·0426	45·9

Amino-acid was absent at the end of these experiments as indicated by the ninhydrin reagent.

Nitrogen Loss by Exposing to Sunlight Ammonium Salt and a Nitrite Solution Mixed with Soil under Sterile Conditions.

In order to find out whether the decomposition of ammonium nitrite solution can take place under sterile conditions, the soil, the ammonium sulphate, the potassium nitrite and a silica boiling tube were sterilised in an autoclave for 2½ hours at 20 lbs. pressure. 25 C.c. of sterile distilled water were added and exposed to sunlight, the mouth of the silica boiling tube was covered with a plug of sterile cotton wool.

0·25 G. of ammoniacal nitrogen as ammonium sulphate and 0·25 g. nitric nitrogen as potassium nitrite were mixed with 50 g. sterile of soil and 25 c.c. of sterile water were exposed to sunlight for 474 hours in the months of January, February and March, 1935. After this

exposure 0·056 g. of NH_3-nitrogen and 0·0422 g. of nitric-nitrogen were left in the soil showing a decomposition of 80% of the nitrogen added. There was a steady evolution of bubbles of nitrogen gas in experiment. Hence it can be concluded that this type of denitrification can take place in the absence of bacteria.

Part played by Organic Manures.

The observations of Lipman and Blair (*Soil Sci.*, 1918, **5**, 291) Clark and Rolley (*ibid.*, 1931, **31**, 299) and Rusell ("Soil Conditions and Plant Growth", 1932, pp. 480-81) seem to indicate that farmyard manure is more effective than artificial manure in plant growth. The part played by organic substances in the soil, has been stated by Russell in the following words:—

"While plants can grow satisfactorily and attain full development with inorganic nutrients only, yet, in natural conditions, their nutrition always proceeds in presence of organic matter. There has been much discussion as to whether this plays an active part in the process. The experimental evidence is not very definite.

In the Rothamsted field experiments, no combination of artificial fertilisers is as effective as farmyard manure in steadying crop yields from year to years, but the effect could readily be attributed to physical and physico-chemical action on the soil."

Lipman and Blair (*loc. cit.*) have stated that analysis of the soil at the end of 20 years' period show that a large part of the nitrogen not recovered from the farm manure is found accumulated in the soil, but there is no accumulation of nitrogen in the plots treated with sodium nitrate.

On the other hand, Prayanishnikov (*Trans. Sci. Inst. Fert. Moscow*, 1930, **73**, 61) has concluded that the results obtained at Rothamsted, Danish and Russian experimental stations show that artificial manures are better than farmyard manure. Investigators in India notably Norris (*Mem. Dept. Agr. India, Chem. Series*, 1923, **6**, No. 8) Viswanath ("Some Aspects of Plant Nutrition", 1932, pp. 13-16) Batham (private communication) and others have shown that farmyard manure is better than a complete mineral manure containing nitrogen, potash and phosphates for a long period of cultivation and that farmyard manure has a residual effect lasting for five years. We are of the opinion that besides the well known influence of organic matter in increasing the colloidal matter and water retention power

of the soil, the carbonaceous matter added to the soil with farmyard and other organic manures markedly retard the oxidation of proteins to ammonia and of ammonium salts to nitrites and nitrates.

In several publications from these laboratories (Compare Dhar "New Conceptions in Biochemistry" 1932, pp. 44-46) it has been shown, that both carbohydrates and fats markedly act as negative catalysts, and retard the oxidation of amino-acids and proteins, and that is why carbohydrates and fats are likely to act as protein sparer in the animal body. Similarly the oxidation of carbohydrates and fats is also retarded by proteins or amino-acids. These results have recently been confirmed by Ghosh and Rakshit (*J. Indian Chem. Soc.*, 1935, **12**, 357). Moreover Willstire (*Z. Physiol.*, 1931, **72**, 88) has shown that the oxidation of adrenaline in presence of enzymes is very considerably retarded by the addition of amino-acids. In the soil also, the carbonaceous substances like cellulose, carbohydrates, fats, added with organic manure retard the oxidation of proteins, amino-acids, and ammonium salts by air and thus act as protectors of the soil nitrogen compounds. It is clear, therefore, that when the carbon content of a soil is high and the nitrogen content low, there will be less oxidation of the soil nitrogen and less chance for the formation and decomposition of ammonium nitrite and less nitrogen loss than when the carbon content is low and nitrogen content high. The foregoing observations, justify the application of organic manures for preserving the nitrogen of soils, specially in tropical countries, where due to sunlight and high temperature, the velocity of the oxidation of the soil organic and inorganic compounds and the decomposition of ammonium nitrite is high and the nitrogenous compounds want more protection than in temperate climates.

Molasses from sugar factories in India are practically wasted now. They should be added to the soil for the fixation of atmospheric nitrogen as has been observed by us (Compare *Proc. Acad. Sci., U. P*, 1934, **4**, 175 ; 1935, **4**, 330), and for the preservation of the soil nitrogenous compounds by decreasing their too rapid oxidation.

Sahasrabudhe and Gokhale (*J. Univ. Bombay*, 1933, **2**, 68) have studied the nitrification of different oil-cakes in medium black, laterite and garden soils and have shown that nitrogen loss occurs and this loss is the greatest with the most easily and quickly nitrifiable cakes.

Heck (*Soil Sci.*, 1931, **31**, 335) has reported that in the conservation of the nitrogen in farm manure, the conditions must be anaerobic and 3/8 to 1/2 of the nitrogen in manure is easily lost by spreading

in warm dry and sunny days. These results are easily explained from the viewpoint advanced in these publications.

The experimental results recorded in this paper show that ammonium sulphate mixed with soil, and exposed to sunlight in the hottest part of the year decomposes to the extent of 60% and in order to minimise this nitrogen loss, which is more pronounced in tropical conditions, the ammonium salts have to be mixed with carbonaceous substances like molasses, green manure, etc. It appears that in the tropics, the value of ammonium salts as manure is enhanced when mixed with carbonaceous substances in order to decrease the velocity of the formation and decomposition of ammonium nitrite. Our results show that molasses not only fixes atmospheric nitrogen when added to the soil but acts as a protector of the soil nitrogen and hence it would prove to be a valuable manure specially in tropical places. Oil-cakes containing fats and nitrogenous compounds can also act in the preservation of the soil nitrogen, because fats are known to retard the oxidation of proteins and amino-acids.

SUMMARY.

1. The velocity of the thermal and photochemical decomposition of an aqueous solution of NH_4NO_2 has been determined at 40° and 50°. The velocity of the thermal decomposition is increased by increase of temperature, but the photochemical velocity is slightly affected by increase of temperature. The ratio of photochemical to the thermal decomposition of NH_4NO_2 is higher at 40° than at 50°, *i.e.*, when the temperature is high, the thermal decomposition of NH_4NO_2 is marked.

2. Copious decomposition of mixtures of $(NH_4)_2SO_4$ and KNO_2 in presence of dry soil and exposed to sunlight in the months of April, May and June, has been observed.

3. Solutions of α-alanine and KNO_2 mixed with soil and exposed to sunlight undergo considerable loss of nitrogen.

4. Sterile solutions of $(NH_4)_2\ SO_4$ and KNO_2 mixed with sterilised soil when exposed to sunlight in quartz boiling tubes show considerable decomposition with evolution of gaseous nitrogen.

5. Organic manures, oil-cakes, green manure, farmyard manure, molasses, etc., produce beneficial results specially in tropical countries not only by increasing the colloidal content and water retention power of the soil, but also protect the soil nitrogen by decreasing the velocity of the formation and decomposition of ammonium nitrite.

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Parachor and Ring Structure. Part II. The Spatial Configuration of Bridged-ring Compounds.

By Susil Kumar Ray.

At first sight it would appear that bridged-rings, *e.g.*, camphor consist of two fused five membered rings having three common atoms. In the fusion of rings with two common atoms, there is no change in the form of either ring, which retains its individual property intact. This is the case with naphthalene, and generally with all the ring systems having two common atoms. The parachor of such ring system is the sum of the parachor of the individual rings, as shown in previous communications (*J. Indian Chem. Soc.*, 1934, **11**, 499, 671). Such is not the case, however, when there are three common atoms in two rings. In these cases the valency angle between the carbon atoms, and hence the amount of strain, must be altered to an appreciable extent and the nature of the rings, at least one, must also be changed. It is expected that parachor value of such ring systems will not be the sum of the parachor of the two separate rings. The object of the present investigation is to find out the parachor contribution of such ring systems and to deduce, if possible, the spatial configuration of such compounds from their parachor values.

In the present paper data are given for fifteen compounds. The surface tension has been determined by the method of maximum bubble pressure, as in the previous works. Two bubblers were employed for every determination and five readings were taken with each. The surface tension was calculated from the mean of these ten readings. The error in any individual determination is much below 1% (the error in the mean value is probably less than 0·5%) and as the fourth root of the surface tension is required in the calculation of the parachor, this error has practically no effect on the parachor value.

The liquids and the solids used were very carefully purified, the former by distillation, generally under reduced pressure and the latter by repeated crystallisations, until there is no change in the boiling point and melting point respectively of the substances.

The observed values of the parachor of these compounds are given in the fourth column of the following tables; the column headed

$\Sigma[P]$ gives the sum of the atomic and structural constants except that for the ring, so that the effect of this structure is obtained by subtracting $\Sigma[P]$ from $[P]_{obs.}$ and is given in the last column.

Reduced Benzene Rings.

TABLE I.

	Temp.	Density.	Surface tension.	$[P]_{obs.}$	$[P]$.	Diff.
*cyclo*Hexane	33°	0·7676	23·94	242·1	234·0	8·1
*cyclo*Hexanone	31°	0·9385	33·59	251·4	243·0	8·4
3-Methyl *cyclo*hexanone	32°	0·9084	30·39	289·6	282·0	7·6
*cyclo*Hexanol	33·5°	0·9393	33·15	255·5	254·0	1·5
	98°	0·8804	25·96	256·4	254·0	2·4
*cyclo*Hexyl acetate	32°	0·9608	30·42	347·0	338·2	8·8
Menthol	98°	0·8399	22·54	404·7	410·0	−5·3
	150°	0·8114	18·38	398·1	410·0	−11·9
Menthol acetate	30°	0·9091	27·98	500·9	493·8	7·7
Dipentene	33·5°	0·8523	27·45	365·3	368·0	−2·7
	97°	0·8021	21·41	364·9	368·0	−3·1

It will be seen from the above table that the parachor contribution of the fully reduced benzene ring is about 8·1. The low value in the case of *cyclo*hexanol may be due to association. In this case the parachor increases with the increase of temperature indicating that the molecules are probably associated. This is further confirmed by studying the corresponding acetate derivative, where this association is prevented and normal parachor value is obtained. For the association between two molecules of a hydroxylic compound Sidgwick and Sutton (*J. Chem. Soc.*, 1930, 1461) observed a parachor decrease of 7·2 per molecule. Adding this to the observed parachor value of *cyclo*hexanol, 8·7 is obtained as the parachor contribution of the *cyclo*hexanol ring, which agrees quite satisfactorily with the mean value. It appears that menthol is also similarly associated. Abnormal result is also obtained in the case of dipentene but here the presence of a double bond in the ring complicates the matter.

It is of great interest to note that the parachor contribution of a *cyclo*hexane ring (8·2) is different from that of the benzene ring (6·1). This is in accord with the modern researches on *cyclo*hexane rings

(Sachse, *Ber.*, 1890, **23**, 1363; *Z. physikal. Chem.*, 1892, **10**, 203; 1893, **11**, 185; Mohr, *J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316), which have definitely shown that a rigid planar structure of such compounds is no longer tenable. Such a bent structure will possess one or other of the following forms:

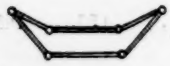

FIG. 1.

FIG 2.

FIG. 3.

The present observed parachors demonstrate strikingly the difference between the benzene and *cyclo*hexane rings and lends additional support to the Sachse structure (*loc. cit.*) from an entirely new standpoint.

Bridged-ring Compounds.

TABLE II.

	Temp.	Density.	Surface tension.	$[P]_{obs.}$	$[P]$.	Diff.
Camphor oxime	130°	0·9526	25·35	402·8	394·4	8·4
	145°	0·9452	24·45	402·4	394·4	8·0
Bromocamphor	80°	1·295	31·93	423·8	415·7	8·1
	96°	1·276	30·19	424·2	415·7	8·5
Camphene	75°	0·8470	23·36	353·1	344·8	8·3
	95°	0·8242	20·97	353·1	344·8	8·3
Borneol acetate	32°	0·9764	29·74	468·8	459·6	9·2
	97°	0·9219	23·37	467·6	459·6	8·0
Fenchone	33°	0·9378	30·11	379·6	364·8	14·8
	98°	0·8867	23·39	377·0	464·8	12·2
	145°	0·8484	19·07	374·4	464·8	9·6
Camphor benzoate	94°	0·9969	28·78	594·8	582·5	12·3
	97°	1·001	29·09	594·6	582·5	12·1
α-Pinene	33°	0·8582	26·13	358·3	344·8	13·5
	97°	0·8050	19·97	357·2	344·8	12·9

It will be noticed from the above table that the parachor contribution of the camphor and similar rings is about 8·4, the only exception being with fenchone.

From the identical parachor contribution of the *cyclo*hexane and the camphor rings, it seems probable that they possess identical configuration. It may be shown with the help of models, that a bridged (1 : 4) ring compound can only be formed from Fig. 1, without involving any strain (*cf.* Fig. 3).

In any other structure certain amount of strain will be involved. It may be expected that there is not much strain in the camphor ring for "nature tries to synthesise strainless compounds." "It will be seen that Fig. 1 is identical with Fig. 3 except that for the bridge. From the identical parachor contribution of the two ring systems, it appears that the camphor ring may be represented by Fig. 3. which has the additional advantage of involving practically no strain. In this connection it is to be assumed that the presence of the bridge in no way interferes with the parachor value of the ring.

Wightman (*J. Chem. Soc.*, 1926, 2541) has shown that Fig. 1 is sufficiently loose to allow of strain-free relative rotations of its carbon atoms and is stereochemically indistinguishable from a plane ring by reason of its mobility. It is expected that there should be no geometrical isomerism in Fig. 1 and hence in Fig. 3, which explains the non-existence of the geometrical isomers of camphor.

The cases of camphor benzoate and pinene become complicated due to the presence of a double bond in the ring, which prevents them from having a structure like *cyclo*hexane. It is probable that in these cases only distortion of the electronic orbits takes place with a certain amount of change in the form of the rings.

I take this opportunity of expressing my thanks to Prof. P. R. Rây of the University College of Science and Prof. A. Maitra of the Presidency College for the kind interest they took in the work which is being continued.

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Studies on Optical Activity and Chemical Constitution. Optically Active Acids and Bases. Part II.

By Mahan Singh and Manohar Singh.

In a previous communication (Singh and Singh, *J. Indian Chem. Soc.*, 1935, **12**, 219) it was shown that the introduction of the dimethylamino group in the *para* position raised the rotatory power of phenyliminocamphor to an enormous extent. We have now prepared *p*-diethylaminophenyliminocamphor and measured its rotatory constants in twelve solvents for three wave-lengths. These values (*vide* experimental) exceed those of the dimethyl compound. The order is, however, practically the same as that for the dimethyl compound in these solvents.

This compound was also examined in benzaldehyde solution and gave an extraordinary low value. It has $[\alpha]_D = 972°$ which fell to $[\alpha]_D = 608°$ after 27 hours.

The dimethyl compound described in Part I (*loc. cit.*) and the diethyl compound are both phototropic and thermotropic. The change in colour of the dimethyl compound is so slight that it escaped notice in the first instance. The changes which these substances undergo are represented by the following schemes:—

p-Dimethylamino compound

Sunlight
Yellow ⟶ Light orange
Dark or heating to 100-105°.

p-Diethylamino compound

Sunlight
Light orange ⟶ Scarlet
Dark or heating to 80-85°

pp'-Bisiminocamphordiphenylamine (Singh, Singh and Lal, *J. Chem. Soc.*, 1921, **119**, 1971) is phototropic as well as thermotropic, but in this case, the changes have been explained by assuming that the hydrogen atom of the amino group oscillates between the two carbonyl groups. This causes the conjugation in the molecule to become continuous and also explains its high rotatory power. In the dialkylaminophenyliminocamphors, however, there exists no possibility of this nature.

Iminocamphor and its aryl derivatives containing an azethenoid group are capable of existing in two stereoisomeric forms, *syn* and *anti*, though numerous derivatives of iminocamphor (Forster and others, *J. Chem. Soc.*, 1909, **95**, 944; Singh and co-workers, *ibid.*, 1919, **115**, 944; 1920, **117**, 980, 1599) exist in one form only (*cf.* *J. Chem. Soc.*, 1910, **97**, 2156; also Singh and Rai, *J. Indian Chem. Soc.*, 1926, **3**, 389). *p*-Dimethyl- and *p*-diethylphenyliminocamphors also show isomerism of this type, the two forms showing different rotatory powers.

The light orange variety of the dimethyl compound and the scarlet variety of the diethyl compound have higher rotatory powers than the corresponding yellow and light orange forms.

Solvent.	*p*-Dimethylphenyliminocamphor.	
	Light orange.	Yellow.
Benzene	2496°	2053°
Toluene	2396	1884
Aniline	3000	2896

The following are the values indicating a progressive change from one variety to the other.

p-Diethyl compound in aniline $[\alpha]_D = 3322° \xrightarrow{2\text{-}3 \text{ hrs.}} 3219°$

$\xrightarrow{6 \text{ hrs.}} 3104° \xrightarrow{2 \text{ days}} 3000°$

" (Scarlet form) in ethyl alcohol $[\alpha]_D = 2982° \xrightarrow{2 \text{ hrs.}}$

$2763° \xrightarrow{2 \text{ hrs.}} 2368° \xrightarrow[\text{sunlight}]{\text{exposed to}} 2675°$

" (Light orange) in ethyl alcohol $[\alpha]_D = 2263° \xrightarrow{2 \text{ hrs.}}$

$2607{\cdot}8° \xrightarrow{\text{in dark}} 2306° \xrightarrow{\text{sunlight}} 2629°$

It is, therefore, clear that an equilibrium mixture is obtained in the solution and in each case the final values approach one another. The substance could not be examined in other solvents as the quantity available was very small.

Experimental.

p-Diethylaminophenyliminocamphor.—Camphorquinone (1·82 g.) and *p*-aminodiethylaniline (1·64 g.) in absolute alcohol solution (25 c.c.) were refluxed on a water-bath for 3 hours with anhydrous sodium sulphate. The dialkylamines decomposed rapidly on exposure and

therefore a considerable amount of tarry matter was produced. The condensation product after cooling was poured into water. The tarry matter was removed after repeated crystallisations from dilute alcohol, when it was obtained as light orange needles, melting at 102·5°, to a deep red coloured liquid, yield 10%. (Found: N, 9·18. $C_{20}H_{28}ON_2$ requires N, 8·97 per cent).

It is readily soluble in methyl or ethyl alcohol, benzene, carbon bisulphide, chloroform and other organic solvents. It dyes wool yellow and in alcoholic solution is an indicator analogous to methyl orange giving with mineral acids a pink and with alkalies a light yellow colour.

Specific rotatory powers of p-*diethylaminophenyliminocamphor.*

Solvent.	Conc.	Temp.	$[\alpha]_D$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.
C_6H_6	0·0120 g./25 c.c.	32°	2292°	2667°	3271
$C_6H_5CH_3$	0·0123	33	2053	2419	3130
C_6H_5Cl	0·0122	32	2623	2848	3627
C_6H_5Br	0·0300	32	2667	2933	3667
$C_6H_5NO_2$	0·0122	33	2848	2869	3484
$C_6H_5NH_2$	0·0152	32	3822	3487	4770
,,	0·0124	32	3104	3467	4596
,,	0·0120	32	3000	3229	4166
C_6H_5CHO	0·0144	34	972		
	After 27 hours		608		
C_5H_5N	0·0135	33	2685	3000	3796
MeOH	0·0146	32	2603	2671	3562
EtOH	0·0120	32	2625	2750	3333
$(CH_3)_2CO$	0·0123	32	2276	2398	3232
$CHCl_3$	0·0120	32	2854	3021	3750
CS_2	0·0128	32	2441	2480	2852

The *p*-aminodiethylaniline used above was prepared by two methods, firstly by the reduction of *p*-nitrosodiethylaniline (*cf.* Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," 1931, p. 387), secondly by the reduction of sodium salt of *p*-sulphobenzeneazodiethylaniline by stannous chloride and hydrochloric acid. The yield in each case was 15-20%.

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Condition of Iodic Acid and Iodates in Aqueous Solution.

By N. R. Dhar and R. N. Mittra.

The ease with which iodic acid becomes converted into iodine pentoxide and the formation of acid salts of iodic acid led J. Thomsen to state in 1874 that "it seems in the highest degree probable that iodic acid is dibasic with the molecular formula $H_2I_2O_6$."

The measurements of freezing point lowering, elevation of boiling points and electrical conductivity carried on by Rosenheim and Liebknecht (*Annalen*, 1899, **308**, 40) and Groschuff (*Z. anorg. Chem.*, 1906, **47**, 33) shows that solutions of iodic acid contain $H_2I_2O_6$.

In a previous paper (Dhar, *J Indian Chem. Soc.*, 1928, **5**, 585) it was pointed out that the precipitation values of iodate ion from iodic acid or from iodates of sodium and potassium on ferric hydroxide sol are comparable with those of divalent ions. Moreover, Bhagwat and Dhar (*ibid.*, 1929, **6**, 781) concluded from their experiments that coagulating power of iodate ion is of the same order as that of a bivalent ion on ceric hydroxide, zirconium hydroxide and ferric hydroxide sols. The recent work of Nayar and Gairola (*Z. anorg. Chem.*, 1934, **220**, 163) on the freezing point lowering and molecular conductivity difference is in favour of partial polymerisation of iodic acid and iodates.

From our experiments on the coagulation of chromium hydroxide, thorium hydroxide and beryllium hydroxide sols the following results are obtained.

Table I.

Chromium hydroxide sol.

		Dialysed soil I.	Dialysed soil II.
Concentration	...	109 g. of Cr_2O_3 per litre	127 g. of Cr_2O_3 per litre.
Amount of chloride	...	32·8 g. per litre	19·8 g. per litre
Purity	...	0·774	1·496
Ppt. conc. of KIO_3	...	0·0125*M*	0·0075*M*
Ppt. conc. of K_2SO_4	...	0·0088*M*	0·0055*M*

TABLE II.

Beryllium hydroxide sol.

Conc.	36·09 g./litre.
Amt. of chloride	35·14 g./litre
Purity	1·44
Ppt. conc. of KIO_3	0·00325*M*
Ppt. conc. of K_2SO_4	0·00325*M*

TABLE III.

Thorium hydroxide sol.

	Dialysed sol I.	Dialysed sol II.
Conc.	11·52 g. of ThO_2 per litre	11·94 g. of ThO_2 per litre
Amt of nitrate	0·133 g./litre	0·0645 g./litre
Purity	20·26	43·25
Ppt. conc of KCl	0·054*M*	0·038*M*
Ppt. conc. of KIO_3	0·0013*M*	0·00125*M*
Ppt. conc. of HIO_3	0·0029*M*	0·004*M*
Ppt. conc. of K_2SO_4	0·00036*M*	0·00026*M*

In order to observe whether potassium iodate in aqueous solution contains $I_2O''_6$ ions, the molecular conductivities of KCl and KIO_3 were compared under identical conditions at 20°. The following results are obtained.

TABLE IV.

Dilutions ...	4	8	16	32	64	128	256	512	1024
Mol. conducty. of KCl	105·6	109·4	111·0	113·0	114·6	115·6	117·4	118·1	119·0
Mol. conducty. of KIO_3	72·8	77·8	81·75	84·9	87·4	88·7	89·6	90·2	90·3

Recently the Raman spectra of iodic acid and alkaline iodates as solids and aqueous solutions have been investigated but no definite conclusions regarding polymerisation of iodic acid and iodates in aqueous solutions can be drawn from the Raman spectra. Nayar and Sharma (*Z. anorg. Chem.*, 1934, **220**, 169) have attributed the band at 634 and 334 to the polymers of iodic acid. But Venkateswaran (*Proc. Indian Acad. Sci.*, 1935, **2**, 119) does not agree with the above authors and advances the view that the line at 823 which is prominent as the component to the band at 779 is due to $I_2O''_6$ ions. Unfortunately this band which is present in solid potassium acid iodate only, cannot be detected in solutions of iodic acid, acid iodates and normal iodates, which from chemical evidence appear to be partially polymerised even in aqueous solutions. Hence it can be concluded that the coagulating power of solutions of iodic acid and iodates on positively charged hydroxide sols and the greater

difference in the molecular conductivities of potassium iodate at dilutions of 1024 and 4 in comparison with potassium chloride are the best evidence supporting the partial polymerisation of iodates and iodic acid in aqueous solutions.

Summary.

1. The coagulating power of aqueous solutions of iodic acid and potassium iodate on the positively charged sols of beryllium hydroxide, chromium hydroxide and thorium hydroxide is much greater than that of potassium chloride and is comparable with potassium salts of dibasic acids.

2. The difference in the molecular conductivities of potassium iodate at dilutions 1024 and 4 is much greater than that of potassium chloride under the same conditions. These results support the view that in aqueous solution iodic acid and iodates are partially polymerised.

3. Evidence of polymerisation of iodic acid and iodates from Raman spectra seems inconclusive.

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Metallic Titanium in Organic Synthesis.

By Vishwa Nath Sharma and Sikhibhushan Dutt.

In continuation of the work on synthetic use of metals published from this laboratory (Ray and Dutt, *J. Indian Chem. Soc.*, 1928, **5**, 103 ; Chakrabarty and Dutt. *ibid.*, 1928, **5**, 517 ; Lal and Dutt, *ibid.*, 1932, **9**, 565 ; Gaind and Dutt, *Allahabad University Studies*, 1934, **4**, 293 ; Lal and Dutt, *J. Indian Chem. Soc.*, 1935, **12**, 389) the metal titanium has now been used for the first time in organic synthesis, since it is now commercially available. The present investigation embodies the results of successful experiments with the metal, while the record of unsuccessful attempts has been avoided for the sake of abbreviation.

As the result of the above investigation it has been found that metallic titanium plays a purely catalytic part in the Zincke's and Friedel and Craft's reactions that have been carried out with the metal, since the yields of the reaction products were found to be independent of the amount of metal used in the reactions. Also a very small amount of the metal was required to start the reaction in most of the reactions. Zincke's reaction gave the most satisfactory result with metallic titanium and the yields obtained in this case were consequently the highest. Ullmann's reaction with metallic titanium was far less satisfactory, and also as in the case of metallic chromium (Chakrabarty and Dutt, *loc. cit.*) titanium also reacted only in those cases where the halogen atom was loosely attached to the organic molecule. Titanium as a neutral reducing agent was also not much of a success. In comparison with the other metals that have been worked up in this laboratory, it has been found that titanium is only slightly more reactive than chromium, but far less reactive than aluminium, thorium or cerium.

Experimental.

Zincke's Reactions with Metallic Titanium.

Action of benzyl chlordie on benzene.—A mixture of dry benzene (50 g.), benzyl chloride (24 g.) and titanium (4·5 g.) was refluxed on the water-bath for 10 hours. The reaction began after 2½ hours and

copious hydrogen chloride was evolved during the rest of the period. The filtered product was fractionated at the ordinary and also reduced pressure and three fractions, *viz.*, (*a*) at 200-270°/755 mm., (*b*) at 200-250°/50 mm., and (*c*) at 250-360°/10 mm. were collected. Fraction (*a*), redistilled at 258-262°, on keeping in a refrigerator, solidified to a mass of radiating needles, m.p. 25-26° and was indentified to be diphenylmethane, yield 9·8 g.

Fraction (*b*) on standing for a few days in the refrigerator, deposited a mass of crystalline matter which on recrystallisation from acetic acid melted at 57° and was identified to be $\alpha\alpha\beta$-triphenylethane, yield 4·2 g. The mother liquor from the above on dilution with alcohol and allowing it to stand for several days deposited another crop of crystals, m p. 67-68° which were identified to be *o*-dibenzylbenzene, yield 0·5 g. The alcoholic mother liquor from the above on evaporation gave a viscid product from which nothing definite could be isolated.

Fraction (*c*) was found to be a complex condensation product of indefinite constitution containing chlorine.

Action of benzyl chloride on naphthalene —The reaction was carried on as above and four fractions were collected at 760 mm. (*a*) up to 250°, (*b*) at 250-320°, (*c*) 320-370° and (*d*) above 370°.

Fraction (*a*) was mainly benzyl chloride and fraction (*b*) mainly naphthalene. Fraction (*c*) was freed from traces of naphthalene by steam distillation and again fractionated, when the greater portion of it came over at 340-355°, and a small portion at 300-320°. Both these fractions solidified on standing and the small fraction on recrystallisation from hot alcohol melted at 39-40°, and was identified to be β-benzylnaphthalene. The greater fraction was crystallised from methyl alcohol in rhombic plates, m. p 57-58° and was identified to be α-benzylnaphthalene. Both these substances on treatment with nitric acid yielded the corresponding phenylnaphthyl ketone, the α-compound melting at 72-73° and the β-compound at 79-80°. The yield of β-benzylnaphthalene was 18 g. and that of α-benzylnaphthalene was 10 g.

Action of benzyl chloride on diphenyl.—The reaction was carried on as usual and the product was extracted with benzene, filtered and the filtrate fractionated at 10 mm. Four fractions were collected (*a*) up to 100°, (*b*) 100-200°, (*c*) 200-250° and (*d*) 250-360°.

Fraction (*a*) was mainly benzyl chloride and diphenyl. Fraction (*b*) was redistilled and the distillate, collected at 150-200°/10 mm.,

was mixed with fraction (*c*) and distilled once again. The fraction collected at 174-180°/10 mm., was a colourless oil which quickly solidified and on crystallisation from acetic acid was obtained in long glistening white needles, m. p. 44-45°. On oxidation with chromic acid in glacial acetic acid, the substance was converted into terephthalic acid and this together with the fact that on analysis it was found to have a formula $C_{19}H_{16}$ confirmed the substance to be *p*-benzyldiphenyl. No other substance could be isolated from the mother liquors or from the fraction (*d*), which remained as a non-crystallisable syrup. All the substances isolated in course of this experiment had very strong floral odours. (Found: C, 93·4 ; H, 6·65. $C_{19}H_{16}$ requires C, 93 44 ; H, 6·56 per cent). The yield of *p*-benzyldiphenyl was 12·4 g.

Action of benzyl chloride on quinol dimethyl ether.—A mixture of benzyl chloride (15 g.), quinol dimethyl ether (25 g.) and titanium powder (4 g.) was refluxed at 130-140° for 8 hours. The product was treated with dilute caustic soda so as to dissolve any demethylated product and then extracted with benzene. After evaporation of the solvent, the product was fractionated at the ordinary pressure and resolved into five fractions: (*a*) below 200°, (*b*) 200-280°, (*c*) 280 320°, (*d*) 320-360° and (*e*) above 360°. Fraction (*a*) was mainly moisture and benzyl chloride, fraction (*b*) was quinol dimethyl ether, fraction (*c*) was a yellow oil changing to deep red on keeping, fraction (*d*) was a red oil and fraction (*e*) was a dark red jelley. Fraction (*c*) on standing for about two months gave a small amount of a pale yellow crystalline substance melting at 104-105°. This product was not noticed by previous workers and was probably dibenzylquinol dimethyl ether, but this could not be confirmed on account of the poor yield. Fraction (*d*), redistilled at 350-360°, was found to be pure benzylquinol dimethyl ether, yield 23·5 g.

Action of benzyl chloride on anisole.—This reaction was brought about in the same way as the one mentioned above. The product on fractionation above 290° yielded three fractions: (*a*) 290 315°, (*b*) 315-345°, and (*c*) 345-380°. Fraction (*a*) redistilled at 303-305° was a very large one and was identified to be anisoylphenylmethane. Fraction (*b*) was a very small one and could not be identified. Fraction (*c*), redistilled at 376-382°, was a pale yellow liquid with an intense greenish-blue fluorescence and was identified to be 2:4-dibenzylanisole. (Found: C, 86·1; H, 7·3. $C_{21}H_{20}O$ requires C, 87·5; H, 7·1 per cent). Yield of the first product was 63% and that of the second 12%.

Action of benzyl chloride on phenetole.—This reaction was also

carried on in a similar way to the above. The product was fractionated and three fractions isolated : (*a*) at 305-315°, (*b*) at 315-345° and (*c*) at 345-360°. Fractions (*a*) and (*b*) were mixed together and redistilled at 330-346° and once again at 338-341°, when a pale yellow oil was obtained which was identified to be *p*-ethoxydiphenylmethane, yield 76%. Fraction (*c*) was a yellowish red oil which on cooling became semi-solid and was probably *dibenzylphenetole* but this could not be confirmed as the product could not be purified sufficiently for analysis.

Action of benzyl chloride on toluene.—This reaction was carried on in the same way as with benzene. The product was fractionated as usual and four fractions were isolated: (*a*) at 100-200°, (*b*) 200-260°, (*c*) at 260-285° and (*d*) at 285-360°. Fraction (*a*) was unchanged benzyl chloride and toluene, fraction (*b*) was very small and was of indefinite composition, fraction (*c*), redistilled at 279-290° and once again at 283-287°, was a colourless oil identified to be *p*-benzyltoluene and fraction (*d*) redistilled at 260-270°/10 mm. was a colourless highly fluorescent oil which appeared to be 2:4-*dibenzyltoluene* from its analysis. (Found: C, 92·4; H, 7·6. $C_{21}H_{20}$ requires C, 92·8, H, 7·2 per cent). (*cf.* Weber and Zincke, *J. Chem. Soc. Abs.*, 1875, *i*, 158). Yield of the first product was 12·8 g. and that of the second was 9·2 g.

Action of benzyl chloride on phenol.—The reaction was carried on as usual and the product on fractionation at the ordinary pressure yielded two main fractions: (*a*) at 310-330° and (*b*) at 360-380°. Fraction (*a*), redistilled at 315-325° and once again at 320-322°, was a colourless non-fluorescent oil with a fine flowery smell and giving no colour reaction with aqueous or alcoholic ferric chloride. It solidified on standing in the refrigerator for nearly a month and then crystallised from alcohol in colourless glistening prisms melting at 83° and was identified to be *p*-benzylphenol, yield 10 g. Fraction (*b*) was found to be insoluble in caustic alkalis and was apparently free from phenolic groups. It was, in all probability, *p-benzylphenol-benzyl ether* but this could not be ascertained for want of authoritative data. It boiled at 364-365° and was a colourless oil with a strong floral odour, yield 1·2 g. (Found: C, 87·1; H, 6·8. $C_{20}H_{18}O$ requires C, 87·5, H, 6·5 per cent).

Action of benzyl chloride on acenaphthene.—This reaction which was also a very vigorous one and was carried in a similar way to the above. The product was extracted with benzene and after evaporation of the solvent it was fractionated at a pressure of 10 mm. Four fractions

were collected, (*a*) at 150-200° a colourless oil, solidifying at once, (*b*) at 200-250° a trace of an oil partially solidifying, (*c*) at 250-300° a colourless oil and (*d*) at 300-360° a red oil. Fraction (*a*) was only unchanged acenaphthene; fraction (*c*), redistilled at 260-270°, partially solidified on treatment with twice its volume of alcohol and the separated crystals on recrystallisation from acetic acid melted at 49° and were identified with *α-benzylacenaphthene* (*cf.* Dwonewaski and Leonbard, *J.Chem. Soc. Abs.*, 1929, *i*, 56). The alcoholic mother liquor from the above on slow evaporation yielded another colourless crystalline substance which on three recrystallisations from acetic acid melted at 110-111° and was identified to be 5-benzylacenaphthene. It gave 5-benzylacenaphthenequionone on oxidation with chromic acid in glacial acetic acid, m. p. 164°, yield of α-benzylacenaphthene was 42%.

Friedel and Craft's Reactions with Metallic Titanium.

Benzophenone from benzoyl chloride and benzene.—A mixture of dry benzene (28 g.), benzoyl chloride (20 g.) and titanium powder (4·2 g) was refluxed on the water-bath for 30 hours. The product was fractionated at the ordinary pressure and the fraction boiling at 280-320° and redistilled at 305-315° was collected. It solidified in the receiver and on crystallisation from alcohol melted at 47° and was identified to be benzophenone, yield 4·2 g.

Acetophenone from acetyl chloride and benzene.—The reaction was carried on in a similar way to the above. The yield from 22 g. of benzene and 16 g. of acetyl chloride was only 1·8 g.

Triphenylchloromethane from benzotrichloride and benzene.—A mixture of benzene (30 g.), benzotrichloride (25 g.) and titanium (6 g.) was refluxed on the oil-bath at 130-40° for 10 hours. The product was extracted with carbon disulphide and after the removal of the solvent it was fractionated at 10 mm. The fraction boiling at 200-250° solidified in the receiver and on recrystallisation from alcohol was obtained in the form of pale yellow needles melting at 104° and were identified to be triphenylchloromethane, yield 2·8 g.

Benzoylbenzoic acid from benzoyl chloride and benzoic acid.—A mixture of benzoyl chloride (15 g.), benzoic acid (12 g.) and titanium (5·4 g.) was refluxed at 150-160° for 16 hours. The product was steam distilled to remove the excess of benzoic acid and then treated

with a slight excess of ammonium hydroxide, which completely precipitated the titanium as hydroxide. The filtrate on concentration and subsequent acidification with hydrochloric acid precipitated the benzoylbenzoic acid, m. p. 127°, yield 4·2 g.

Ullmann's Reaction with Titanium Metal.

Diphenyl ether from phenol and bromobenzene.—A mixture of phenol (15 g.), bromobenzene (20 g.), potassium carbonate (5 g.) and titanium was refluxed at 180-200° for 15 hours. The reaction product was filtered and extracted with ether and the ethereal extract washed with dilute caustic soda. After the removal of the solvent, the product was fractionated and the fraction boiling at 250-252° was isolated. It was a pale yellow oil with a fine flowery odour and was identified to be diphenyl ether, yield 2·4 g.

Diphenylamine from bromobenzene and aniline.—This reaction was carried on in the usual manner and the yield obtained was only about 8% of the theoretical. When iodobenzene was substituted in place of bromobenzene, the yield improved to about 12%.

Succinic acid from sodium chloracetate and sodium acetate.—This reaction was carried on in the same way as in the case of cerium (Lal and Dutt, *loc. cit.*) and the yield obtained was 24%.

Diethyl succinate from ethyl chloracetate and ethyl acetate.—This reaction was carried on in the same way as above and the yield of the reaction product was about 35%.

Hexanitrodiphenyl from picryl chloride.—A mixture of picryl chloride (10 g.) and titanium powder (4 g.), was heated at 140-150° for 15 hours. The product was extracted with benzene, the benzene extract repeatedly washed with a strong solution of caustic soda and then with water until the washings were colourless and finally the benzene was evaporated, when a brownish yellow crystalline mass was obtained On recrystallisation from alcohol it was obtained in bright yellow needles, m. p. 238° and was identified to be hexanitrodiphenyl, yield was only 0·91 g.

Reformatsky's reaction with titanium powder.—This reaction was carried on in the same way as in the case of cerium (Lal and Dutt, *loc. cit.*) with acetophenone and bromacetic ester and the product identified to be *β-phenylmethyl hydroxypropionic ester*, yield 2·1 g.

Neutral reduction with titanium powder.—Neutral reductions with titanium powder were not very satisfactory, since in each case the yield was very low. The reductions were carried on according to the method of Lal and Dutt.

Picramic acid from picric acid.—The yield was only 0·5 g. from 2 g. of picric acid. *Benzhydrol from benzophenone.*—The yield was 0·66 g. from 2 g. of benzophenone. *o-Aminophenol from o-nitrophenol.*—Yield was 0·2 g. from 2 g. *Aniline from nitrobenzene.*—The yield was 3 g. from 10 g.

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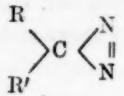
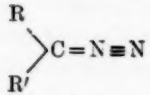
Parachor and Chemical Constitution. Part IV. The Structure of Aliphatic Diazo-compounds.

BY SUSIL KUMAR RAY.

Inspite of much work done by various investigators for more than fifty years, the constitution of the aliphatic diazo-compounds has not yet been definitely settled. Curtius (*Ber.*, 1883, **16**, 2230), who discovered these compounds, proposed the structure (I) while Angeli (*Atti. R. Accad. Lincei*, 1907, *ii* **16**, 790) first pointed out that the reactions of these compounds are best represented by the structure (II)



(I)



(II)

which was further advocated by Thiele (*Ber.*, 1911, **44**, 2552). Both the ring structure of Curtius and the open-chain structure of Angeli-Thiele, have been supported by different investigators from time to time, and it is not possible from a perusal of the literature on the subject to arrive at a definite conclusion. The reactions which these compounds undergo can be explained equally well by means of either the Curtius or the Angeli-Thiele formula. These facts led the present author to attempt at a solution of the problem by determining the parachor of these compounds, the difference in the parachor between the two forms being sufficiently large for a definite decision to be possible by each measurement. It was noted by many investiga-

tors that these compounds gradually change their colour on heating, the original colour reappearing on cooling. All these facts point out that these substances are probably equilibrium mixtures of the two forms, the proportion of the either form present may possibly depend on temperature. The present work was undertaken to find out the parachor of these compounds at different temperatures in order to determine their constitution and to find out whether it depends on the temperature.

In the present paper data are given for four diazo-acetic esters at five different temperatures for each. The surface tension was determined by the method of maximum bubble pressure as in the earlier works.

The compounds were prepared by the method of Curtius (*loc. cit.*). The purification of the impure diazo compounds offered considerable difficulty. Steam distillation (except in the case of the methyl ester) in small quantities, as recommended by Curtius, was found to be the best method of purification, although a large part of the diazo compound is lost thereby. The compounds were finally purified by distillation under low pressure. As the action of light changes these substances to a greater or less extent, all the operations are to be performed in very dim light. These compounds are also decomposed on keeping, hence observations should be made only with freshly prepared samples. Even on keeping for a few hours the surface tension was found to change appreciably.

The observed values of the parachor are given in the fourth column of the following tables, the calculated parachors for the different forms are also given therein.

TABLE I.

Diazo-acetic methyl ester.				*Diazo-acetic ethyl ester.*			
$P_{calc.}$ for ring = 207·7 and for open = 237·6.				$P_{calc.}$ for ring = 246·7 and for open = 276·6.			
Temp.	Density.	Surface tension.	$P_{obs.}$	Temp.	Density.	Surface tension	$P_{obs.}$
0°	1·191	37·51	207·8	0°	1·111	35·00	249·0
20°	1·173	35·36	207·9	20°	1·080	32·05	251·2
30°	1·148	34·86	211·6	30°·5	1·064	31·45	253·7
60°	1·098	33·01	218·3	60°	0·9891	28·25	265·7
80°	1·049	29·72	222·6	99°	0·9679	24·13	261·1

TABLE II.

Diazo-acetic n-propyl ester.				*Diazo-acetic n-amyl ester.*			
$P_{calc.}$ for ring = 285·7 and for open = 315·6.				$P_{calc.}$ for ring = 363·7 and for open = 393·6.			
Temp.	Density.	Surface tension.	$P_{obs.}$	Temp.	Density.	Surface tension	$P_{obs.}$
−5°	0·9954	30·15	301·3	−5°	0·9216	27·85	387·6
0°	0·9896	30·32	303·5	0°	0·9164	27·26	389·0
20°	0·9688	28·90	306·3	20°	0·8847	25·01	394·3
28°	0·9616	28·32	3 7·0	28°·5	0·8778	24·40	395·0
60°	0·9260	25·07	309·3	60°	0·8497	21·36	394·7
90°	0·8921	22·34	312·0	98°	0·8177	20·07	403·8

It will be evident from the above tables, that the parachor of the diazo-acetic esters vary with temperature, the value increasing as the temperature is raised. The values above 90° are not very accurate as the compounds are found to decompose to a certain extent on prolonged heating. From the variation of the parachor with temperature it may be definitely said that these compounds are equilibrium mixtures of the two forms. In low temperatures, the tendency is towards the formation of the ring forms while high temperature favours the open-chain structures. At the ordinary temperatures, the value is generally between the values for the two forms. In this connection it should be noted that the increase in the molecular weight of the alcohol radicle of the esters favours the openc-hain formation.

After the completion of the present work, it was noticed that Lindermann, Wolter and Groger (*Ber.*, 1930, **66**, 702) determined the parachor of some of the aliphatic diazo-compounds. They observed the parachor at a single temperature and as their values in the majority of ca-es were found to lie between the values for the two forms, they concluded that these compounds are probably equilibrium mixtures of the two forms. The work carried out by the present author, extending over a wide range of temperature, has definitely settled this point.

In conclusion the author begs to express his thanks to Prof. P. R. Rây of the University College of Science and to Prof. A. Maitra of the Presidency College for their kind interest in the work.

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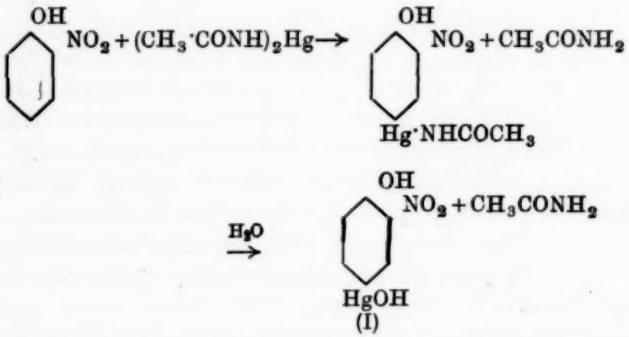
Mercury Acetamide as a Mercurating Agent. Part II. Mercuration of Phenols.

By Kuverji Gosai Naik and Bansidhar Vithaldas Mehta.

Since mercury acetamide has been found to be an effective reagent in the mercuration of cyanoacetamides (Naik and Shah, *J. Indian Chem. Soc.*, 1931, **8**, 29), it was proposed to extent its use in the mercuration of some phenols and examine how far it resembled mercuric acetate in its mercurating action. With this end in view, the interaction of mercury acetamide with *o*-nitrophenol, *p*-nitrophenol, α-naphthol, β-naphthol, and phloroglucinol was studied.

In all cases monohydroxymercuri derivatives were obtained, except in the case of phloroglucinol, which gave a trihydroxymercuri derivative. The reaction in the case of *o*-nitrophenol may be represented as follows:



(I)

Similarly *p*-nitrophenol, β-naphthol, α-naphthol and phloroglucinol gave 2-hydroxymercuri-4-nitrophenol (II), 1-hydroxymercuri-β-naphthol (III), 4-hydroxymercuri-α-naphthol (IV), and 2:4:6-trihydroxymercuri-phloroglucinol (V) respectively. The constitutions assigned to the compounds follow from their reactions with bromine, whereby the HgOH group is substituted by Br.

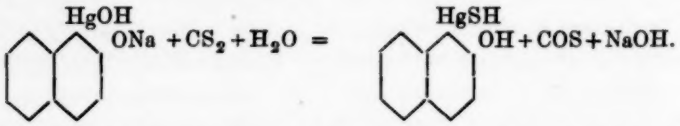
Compounds (I), (II), (III), and (IV) dissolve in dilute sodium hydroxide solution giving hydroxymercuri sodium-phenolates. Compound (V) is insoluble in sodium hydroxide. Dilute hydrochloric acid has no

action on compounds (I) and (II), but concentrated hydrochloric acid decomposes them giving mercuric chloride and the original phenols. Compounds (III) and (IV) are easily decomposed by dilute hydrochloric acid while compound (V) dissolves undecomposed in concentrated hydrochloric acid and can be reprecipitated on dilution.

Compounds (I), (II) and (V) are not affected by hydrogen sulphide, while compounds (III) and (IV) first form a yellow product, which decomposes slowly into mercuric sulphide. Similarly (I) and (II) are not attacked by potassium iodide, whereas (III) is completely decomposed giving a quantitative yield of potassium hydroxide.

$$R{\cdot}HgOH + 2KI + H_2O = R{\cdot}H + HgI_2 + 2KOH.$$

1-Hydroxymercuri-β-naphthol, when dissolved in just the necessary amount of sodium hydroxide and shaken with carbon disulphide, gave β-naphthol-1-mercuri-mercaptan:



Such a course of reaction is not at all uncommon, since similar compounds have been obtained by Koten and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2754) from aryl and alkyl mercuric hydroxides in presence of traces of alkali on shaking with carbon disulphide. When compounds (I) and (II) were similarly treated, a very small amount of a product separated, which was insufficient for analysis. *o*- and *p*-Hydroxymercuriphenols, prepared by the method of Whitmore and Middleton (*J. Amer. Chem. Soc.*, 1921, **43**, 622), when similarly treated, gave bulky precipitates of phenol-*o*- and *p*-mercuric mercaptans respectively.

Sodium thiosulphate is a reagent most generally used for converting the organo-mercury compounds of the type R·HgX to the compounds R_2Hg (Pesci, *Gazzetta*, 1899, *i*, **29**, 394; Dimroth, *Ber.*, 1902, **35**, 2855; Kharasch and Piccard, *J. Amer. Chem. Soc.*, 1920, **42**, 1861, *et seq.*). 2-Acetoxymercuri-4-nitrophenol, when treated with this reagent, gave 2:2′-mercuri-bis-4-nitrophenol.

Experimental.

4-Hydroxymercuri-2-nitrophenol (I).—A hot solution of mercury acetamide (3·2 g.) in dilute alcohol (1:1) was added to *o*-nitrophenol

(1·4 g.) dissolved in the same solvent and the mixture heated for 4 hours on a water-bath, when a granular orange coloured product separated. This was filtered and washed with water, alcohol and ether. It is practically insoluble in all organic solvents, but is soluble in dilute sodium hydroxide and acetic acid. The pure product turns dark above 248° but does not melt till 285°. (Found: Hg, 55·92; N, 4·14. $C_6H_5O_4NHg$ requires Hg, 56·34; N, 3·94 per cent).

Action of bromine.—About 1 g. of the above compound was suspended in water and bromine dissolved in a solution of potassium bromide was added. When the colour of bromine was no more absorbed, it was warmed gently on a sand-bath. On cooling crystals appeared, which were filtered and washed with water. It was crystallised twice from dilute alcohol. The pale yellow needles melt at 88°. It is identical with 4-bromo-2-nitrophenol obtained by Dahmer (*Annalen*, 1904, **333**, 353).

Action of hydrochloric acid, potassium iodide, hydrogen sulphide and ammonium sulphide.—4-Hydroxymercuri-2-nitrophenol, when heated with dilute hydrochloric acid, remained unchanged. When it was heated with concentrated hydrochloric acid it went into solution, which on cooling gave crystals. After recrystallisation, it was identified as *o*-nitrophenol, m. p. 45°.

When boiled with a solution of potassium iodide in water 4-hydroxymercuri-2-nitrophenol remained unchanged. No change was noticed when hydrogen sulphide and ammonium sulphide were added to the aqueous suspension of the above compound.

2-*Hydroxymercuri*-4-*nitrophenol* (II) was prepared by mixing equimolecular proportions of mercury acetamide and *p*-nitrophenol, dissolved in a hot aqueous alcoholic solution and keeping for 24 hours. The yellow product, which separated, was filtered and washed with distilled water, alcohol and ether. It darkens above 248° but does not melt till 285°. (Found: Hg, 56·16; N, 4·09. $C_6H_5O_4NHg$ requires Hg, 56·34; N, 3·94 per cent). When treated with bromine as in the preceding case, it gave a compound, m. p. 113-14°, which was identified as 2-bromo-4-nitrophenol, prepared by Diels and Bunzl (*Ber.*, 1905, **38**, 1491).

2-*Acetoxymercuri*-4-*nitrophenol* was obtained by adding 25 c. c. of glacial acetic acid to 2 g. of compound (II) and heating for 10 minutes. It turns dark above 240° but does not melt till 285°. (Found: Hg, 50·01. $C_8H_7O_5NHg$ requires Hg, 50·38 per cent).

2 : 2'-*Mercuri-bis*-4-*nitrophenol*. — 2-Acetoxymercuri-4-nitrophenol (2 g.) was added to a solution of sodium thiosulphate (1·3 g.) in water. The compound went into solution which deposited a sulphur yellow product after 5 days. It turns dark brown above 190° but does not melt till 285°. (Found: Hg, 41·70. $C_{12}H_8O_6N_2Hg$ requires Hg, 42·02 per cent).

1-*Hydroxymercuri*-β-*naphthol* (III) was obtained similarly from equimolecular quantities of β-naphthol and mercury acetamide dissolved in a mixture of alcohol and water (2:1), m. p. 210° (decomp.). (Found: Hg, 55·48. $C_{10}H_8O_2Hg$ requires Hg, 55·55 per cent). When heated with dilute hydrochloric acid it gave β-naphthol (m. p. 122°) and when treated with bromine as in the preceding case it gave 1-bromo-β-naphthol, m. p. 84° (Smith *J. Chem. Soc.*, 1879, **35**, 789). When suspended in water and treated with hydrogen sulphide for 12 hours it gave black mercuric sulphide.

0·1804 G. of the above compound was added to a solution of potassium iodide (2 g.) in water and boiled for 1 hour. The alkali liberated was equivalent to 14·6 c. c. of 0·0686 *N*-hydrochloric acid, showing that 1·99 equivalents of alkali were liberated and that the splitting of C-Hg linkage was quantitative.

1-*Acetoxymercuri*-β-*naphthol* was prepared by dissolving it in hot acetic acid solution. It melted at 185°. (Found: Hg, 49·64. $C_{12}H_{10}O_3Hg$ requires Hg, 49·75 per cent).

Action of carbon disulphide on compound (III).—A solution of 2 g. of this compound in just the necessary amount of dilute sodium hydroxide when shaken with 2 c. c. of carbon disulphide, gave a yellow product, which blackens above 145° but does not melt till 285°. (Found: Hg, 52·71; S, 8·35. $C_{10}H_8OSHg$ requires Hg, 53·19; S, 8·51 per cent).

4-*Hydroxymercuri*-α-*naphthol* (IV) was prepared in the usual way from mercury acetamide and α-naphthol. It darkens gradually above 240° but does not melt till 285°. (Found: Hg, 55·11. $C_{10}H_8O_2Hg$ requires Hg, 55·55 per cent). On treatment with bromine in a solution of potassium bromide in water it gave a product, m. p. 128° identified as 4-bromo-α-naphthol prepared by Reverdin and Kauffmann (*Ber.*, 1895, **28**, 3054).

Trihydroxymercuriphloroglucinol (V) was obtained on mixing phloroglucinol (1 mol.) and mercury acetamide (3 mols.) dissolved in hot water. It turns brown at 185° and then gradually blackens but does not melt till 285°. (Found: Hg. 76·99. $C_6H_6O_6Hg_3$ requires Hg,

77·52 per cent). On treatment with bromine as in the preceding cases tribromophloroglucinol, m. p. 153°, (Zincke and Kegek, *Ber.*, 1890, 23, 1732) was obtained.

Phenol-o-mercurimercaptan.—A solution of *o*-chloromercuriphenol (2 g) in just the necessary amount of sodium hydroxide, was shaken with 2 c. c. of carbon disulphide, when the mercaptan separated out as a yellow compound. It blackens above 130° but does not melt till 285°, (Found: Hg, 60·85; S, 9·59. C_6H_6OSHg requires Hg, 61·34; S, 9·81 per cent).

Phenol-p-mercurimercaptan was prepared in the same way as above from *p*-chloromercuriphenol. It blackens above 150°. (Found: S, 9·51. C_6H_6OSHg requires S, 9·81 per cent).

The authors are indebted to the Government of H. H. The Maharaja Gaekwad of Baroda for the grant made to enable them to carry out this investigation.

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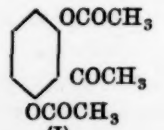
Action of Acetic Anhydride on 2-Acetylresorcin. A New Method for the Synthesis of γ-Resorcylic Acid.

By Dattatraya Balkrishna Limaye and Govind Ramchandra Kelkar.

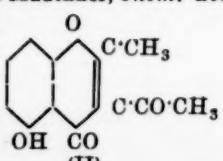
Though the 4-acyl derivatives of resorcin have been extensively studied the 2-acylresorcins were not known until quite recently. A number of 2-acylresorcins have become easily available since the development of the *Nidhone* Process (Limaye, *Ber.*, 1934, **67**, 12). The presence of an OH group on either side of the acyl radical makes the compounds amenable to various reactions. The present communication deals with the reaction of acetic anhydride on 2-acetylresorcin, a typical member of the series (Limaye, *loc. cit.*; Limaye and Cangal, *Proc. Indian Science Congress*, 1934, p. 229) which has been prepared from 8-acetyl-4-methylumbelliferone, m.p. 168°. (Limaye, *Ber.*, 1932, **65**, 375) by the application of the Nidhone Process.

On treatment with acetic anhydride alone, the 2-acetylresorcin yields its diacetate (I). When the condensation is carried out in the presence of sodium acetate, however, the reaction takes a different course and three substances have been isolated from the reaction product under conditions described in the experimental part. One of these melts at 122° and has been found to be 2-methyl-3-acetyl-5-hydroxychromone (II). The other substance, m.p. 109°, is the acetate of the chromone mentioned above. The third substance, which appears to be the corresponding coumarin of m.p. 261-62°.

The constitution of the chromone, which will be fully dealt with in a separate communication along with its other properties, is arrived at from its analysis and its easy hydrolysis with alkali which yields acetone, acetic acid, and γ-resorcylic acid. The latter acid was first prepared by Senhofer and Brunner (*Sitzungber. k. Akad. Wiss. Wien.* 1879, **80**, II, 504, 514; *cf.* also Mauthner, *Chem. Zentrl.*, 1930, **1**, 2881).



(I)



(II)

The hydrolysis of the 2-methyl-3-acetyl-5-hydroxychromone furnishes an excellent preparative method for γ-resorcylic acid as judged from its purity and yield.

Experimental.

Diacetate of 2-acetylresorcin.—The reaction mixture obtained by heating 2-acetylresorcin (1 g.) and acetic anhydride (3 c.c.) at 140°-150° for 3 hours was poured into water and extracted with ether. The ether layer was first washed with dilute caustic soda and then with water. The diacetate obtained on evaporating off the ether was distilled at 175°-180°/10 mm. since it decomposes at about 320° under ordinary pressure. (Found: C, 61·1; H, 5·1. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1 per cent).

2-Methyl-3-acetyl-5-hydroxychromone.—2-Acetylresorcin (1 g.) was heated with sodium acetate (1 g.) and acetic anhydride (2 c.c.) at 160° for 5 hours. The contents of the flask solidified to a brown powder on pouring in excess of water. It crystallises from acetic acid (20 %) in colourless crystals, m.p. 122°, yield 1 g. It is easily soluble in alcohol, benzene and acetic acid and difficultly soluble in water. It is slightly volatile with steam. Its solution in alcohol gives a violet colouration with ferric chloride. (Found: C, 65·9; H, 4·7. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6 per cent).

A product melting at 261°-62° was obtained from the acetic acid mother liquor in a very small amount.

The *acetyl derivative.*—The above chromone was boiled with sodium acetate (1 g.) and acetic anhydride (7 c.c.) at 140°-150° for 3 hours. The product obtained on pouring into water was washed with dilute caustic alkali and then crystallised from boiling water, m.p. 109°, yield 0·5 g. (Found: C, 64·4; H, 4·6. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6 per cent).

It was also obtained from 2-acetylresorcin directly by using sodium acetate and an excess of acetic anhydride.

Hydrolysis of 2-methyl-3 acetyl-5-hydroxychromone.—The chromone (5·5 g.) was boiled with 50 c.c. of 1*N*-caustic soda for about 1 hour under a reflux condenser, and the solution distilled, when acetone was identified in the distillate. The residual solution in the flask was then cooled and acidified with dilute sulphuric acid and the precipitate dissolved in sodium carbonate solution and reprecipitated by hydrochloric acid. On crystallisation from water (charcoal) the product

melts at 166°-67° (decomp.) with a change at about 110° due to removal of the water of crystallisation. It was identified as γ-resorcylic acid directly and through its derivatives. It gives a blue colouration with ferric chloride solution When kept over sulphuric acid in vacuum it loses its water of crystallisation. (Found: C, 48·6; H, 4·8; H_2O, 9·7; equiv., 173. $C_7H_6O_4,H_2O$ requires C, 48·8; H, 4·6; H_2O, 10·4 per cent. equiv., 172).

The filtrate containing sulphuric acid was distilled and acetic acid was easily identified in the distillate.

The preparation of *γ-resorcylic acid* in good yield was effected by boiling 2 methyl-3-acetyl-5-hydroxychromone (1 mol.) with 0·5 *N*-caustic soda solution (2 mols.) for ½ hour and acidifying the resulting solution with hydrochloric acid when major part of the γ-resorcylic acid was precipitated. A further quantity of the acid was obtained by extracting the filtrate with ether, yield 7·6 g. from 11 g. of the chromone.

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Synthesis of Coumarins from Phenols and β-Ketonic Esters. Part V. Constitution of Chlororesorcin and Chlororesorcylaldehyde.

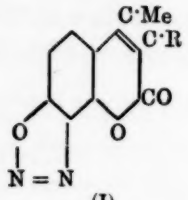
By Dukkhaharan Chakravarti and Baidyanath Ghosh.

Reinhard (*J. pr. Chem.*, 1878, *ii*, **17**, 336) prepared a chlororesorcin by the action of sulphuryl chloride on a dry ethereal solution of resorcin. It is not possible to determine the position of the Cl atom by preparing the chlororesorcin from the two nitroresorcins (*e.g.* 2-and 4-nitroresorcin) as the action of sodium nitrite on a cooled solution of 2-aminoresorcin hydrochloride leads to the formation of a nitroso derivative (Kauffmann and Pay, *Ber.*, 1906, **39**, 323) and as diazotised 4-aminoresorcin, when submitted to Sandmayer's reaction, gives resorcinol-azochlororesorcinol (Voroschov and Gorkov, *J. Gen. Chem. Russ.*, 1932, **2**, 421). Clark (*J. Amer. Chem. Soc.*, 1933, **55**, 319) has recently proved the structure of chlororesorcin to be 4-chlororesorcin by nitrating chlorobenzene and replacing the nitro groups by OH groups *via* the diazo-reaction.

The condensation of halogenated and negatively substituted phenols with β-ketonic esters forming substituted coumarins has also furnished a ready means for determining the constitution of substituted phenols and their derivatives.

Chlororesorcin condenses with acetoacetic ester and its *C*-methyl derivative to form 6-chloro- or 8-chlorocoumarins (Chakravarti and Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 622). The nitration of β methylumbelliferone (*cf.* Pechmann and Cohen, *Ber.*, 1901, **34**, 666) and of 3:4-dimethylumbelliferone gives 8-nitro derivatives as they are identical with the condensation products of 2-nitroresorcin with acetoacetic ester and its *C*-methyl derivative (Chakravarti and Ghosh, *loc. cit.*). Pechmann and Cohen (*loc. cit.*) record the m.p. of the acetyl derivative of nitro-β-methylumbelliferone as 165°. This seems to be inaccurate as the acetyl derivative melted at 198°, and on deacetylation with 20% sulphuric acid it gave the original nitroumbelliferone melting at 256°. 8-Nitroumbelliferones on reduction with stannous chloride and hydrochloric acid gave 8-aminoumbelliferones which formed stable diazoanhydrides (I). The

diazoanhydrides on treatment with cuprous chloride in hydrochloric acid gave 8-chloroumbelliferones which are different from the condensation products of chlororesorcin with acetoacetic esters.



(I)

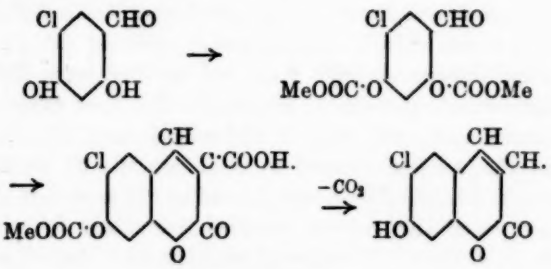
The condensation products of chlororesorcin with acetoacetic esters are, therefore, not 8-chloroumbelliferones but 6-chloroumbelliferones. Chlororesorcin is, therefore, 4-chlororesorcin, as has been shown by Clark (*loc. cit.*). It is rather strange that Lichoscherstov and Tzimbalist (*J. Gen. Chem. Russ.*, 1933, **3**, 162) describe the chlororesorcin (b. p. 259·5°, m. p. 102·5°) obtained by the chlorination of resorcin in presence of dichlorocarbamide as 4-chlororesorcin and identical with Reinhard's product, though Reinhard's product melts at 89° and boils at 259° (Reinhard, *loc. cit.*; Clark, *loc. cit.*).

The singular behaviour of 7-hydroxy-4-methylcoumarin and 7-hydroxy-3:4-dimethylcoumarin in forming 8-nitro derivatives in preference to 6-nitro derivatives is noteworthy. Coumarin itself, however, on nitration gives a mixture of 8-nitro- and 6-nitro derivatives, the latter being largely in excess (*cf.* Dey, *J. Indian Chem. Soc.*, 1927, **4**, 198). 7-Hydroxycoumarin (umbelliferone), however, on nitration, has been found to give a mixture of 8-nitro- and 6-nitro derivatives. The two products have been separated by crystallisation from glacial acetic acid, one melting at 245° and the other at 220°. Clayton (*J. Chem. Soc.*, 1910, **97**, 1400) described the nitration of umbelliferone and isolated a product (m. p. 245°) which was shown by analogy with the nitro derivative of 4-methylumbelliferone (Pechmann and Cohen, *loc. cit.*) to be 8-nitroumbelliferone.

The product melting at 245° has now been proved to be 8 nitroumbelliferone in the following way: On reduction it gave aminoumbelliferone, which formed a soluble diazoanhydride and finally gave a chlorocoumarin (m. p. 263°) by treatment with cuprous chloride and hydrochloric acid, which was different from 6-chloroumbelliferone (m. p. 271°) obtained by malic acid condensation from 4-chlororesorcin. Hence the chloroumbelliferone obtained from nitroumbelliferone is

8-chloroumbelliferone and the nitroumbelliferone is 8-nitro derivative. A direct method of synthesising 8-nitroumbelliferone by the condensation of 2-nitroresorcin with malic acid resulted in failure as 2-nitroresorcin was very easily sulphonated. Hence in the nitroumbelliferone, described by Clayton, the nitro group is in position 8, though Weiss and Kratz (*Monatsch.*, 1929, **51**, 386) are doubtful about the position of the nitro group, as it is not identical with the nitroumbelliferone (m. p. 228°) prepared by them by the action of ethyl ethoxymethylene malonate on 2-nitroresorcin in presence of alcoholic sodium ethoxide.

The formation of a coumarin from chlororesorcylaldehyde (Gattermann. *Annalen*, 1907, **357**, 313) by its condensation with malonic acid has settled the position of substituents in chlororesorcylaldehyde. Chlororesorcylaldehyde, prepared in the present investigation by Roger Adam's modification of Gattermann's reaction, does not condense with malonic acid and attempts to condense the dicarbomethoxychlororesorcylaldehyde with malonic acid in pyridine solution in presence of piperidine also failed. The dicarbomethoxy derivative, however, condensed with malonic acid in glacial acetic acid solution (*cf.* Späth, *Monatsch.*, 1920, **41**, 271 ; Mitter and Saha, *J. Indian Chem. Soc.*, 1934, **11**, 262) yielding a mixture of 2:4-dicarbomethoxycinnamic acid (traces only) and carbomethoxychloroumbelliferone carboxylic acid. The latter, when boiled with sodium carbonate solution, gave chloroumbelliferone carboxylic acid (m. p. 284°), which on heating yielded chloroumbelliferone (m. p. 271°) identical with the condensation product of chlororesorcin and malic acid, *i.e.*, 6-chloro-7-hydroxycoumarin. Hence, chlororesorcylaldehyde is 5-chlororesorcylaldehyde, the reaction taking place as follows:



EXPERIMENTAL.

8-Chloro-4-methylumbelliferone.—The diazoanhydride of 8-amino-4-methylumbelliferone (5 g., Pechmann and Cohen, *loc. cit.*) was

dissolved in the least quantity of concentrated hydrochloric acid and the solution added in the cold to cuprous chloride solution (prepared by adding 100 c.c. of concentrated hydrochloric acid to 10 g. of copper carbonate and heating with copper turnings till colourless). The reddish precipitate obtained was washed with concentrated hydrochloric acid and then with water. It was finally crystallised from glacial acetic acid as light yellow prisms, m. p. 267°. (Found: Cl, 16·24. $C_{10}H_7O_3Cl$ requires Cl, 16·8 per cent).

The *acetyl* derivative, prepared by heating the substance with acetic anhydride and sodium acetate, crystallised from alcohol as colourless prisms, m. p. 188 89°. (Found: Cl, 13·9. $C_{12}H_9O_4Cl$ requires Cl, 14 05 per cent). The condensation product of chlororesorcin and acetoacetic ester, however, melts at 280° (acetyl derivative, m. p. 168°, *cf.* Chakravarti and Ghosh, *loc. cit.*).

8-*Nitro*-3:4-*dimethylumbelliferone*.—To a solution of dimethylumbelliferone (20 g., condensation product of resorcin with methyl acetoacetic ester) in concentrated sulphuric acid (100 c.c.), cooled in a freezing mixture, a mixture of nitric acid (*d* 1·52, 6 c.c.) and concentrated sulphuric acid (12 c.c.) was added drop by drop and the solution mechanically stirred. Stirring was continued for 1 hour more. The mixture was poured into ice-water and the yellow precipitate was filtered and crystallised from glacial acetic acid as yellow prisms, m. p. 260°, yield 14 g. It was proved to be identical with the product obtained by the condensation of 2-nitroresorcin and methylacetoacetic ester by mixed m. p. and also by the identity of their acetyl derivatives (m. p. 198°, Chakravarti and Ghosh, *loc. cit.*).

8-*Amino*-3:4-*dimethylumbelliferone*.—8-Nitro-3:4-dimethylumbelliferone (11 g.) was mixed with stannous chloride (35 g.), concentrated hydrochloric acid (30 c.c.) and rectified spirit (30 c.c.). The mixture was heated on a wire-gauge till a clear solution was obtained, when more concentrated hydrochloric acid (60 c.c.) was added and the solution allowed to cool, crystals of double salt separated after 1 hour. These were filtered and dissolved in the least quantity of water and tin was removed completely by means of sulphuretted hydrogen. The filtered solution was then heated and sodium acetate added when the amino-umbelliferone separated, which was collected and crystallised from dilute alcohol as light greenish-yellow needles, m. p. 272°, yield 5 g. (Found: N, 6·7. $C_{11}H_{11}O_3N$ requires N, 6·8 per cent).

The *diazoanhydride* was obtained by adding in the cold a solution of sodium nitrite (1·2 g.) to a solution of 8-amino-7-hydroxy-3:4-dimethylcoumarin (3·5 g.) in hydrochloric acid (10 c.c. of concentrated hydrochloric acid and 150 c.c. of water). A reddish yellow precipitate was obtained, which was collected and crystallised from hot water in red shining needles, m.p. 172°, yield 3 g. (Found: N, 12·9. $C_{11}H_8O_3N_2$ requires N, 12·96 per cent).

8 *Chloro-3:4-dimethylumbelliferone*.—The diazoanhydride was dissolved in the least quantity of concentrated hydrochloric acid and the solution added to cooled cuprous chloride solution prepared as before. The solution was stirred, when nitrogen was given off and a red precipitate separated. It was washed with water and crystallised from glacial acetic acid as small colourless prisms, m.p. 272°, the m.p. being considerably depressed when mixed with the condensation product of chlororesorcin with methyl acetoacetic ester (m.p. 248°, Chakravarti and Ghosh, *loc. cit.*) (Found: Cl, 15·51. $C_{11}H_9O_3Cl$ requires Cl, 15·8 per cent).

8-*Nitroumbelliferone* and 6-*nitroumbelliferone*.—To the cooled solution of umbelliferone (25 g.) in concentrated sulphuric acid (140 c.c.), which was mechanically stirred, a mixture of nitric acid (*d* 1·52, 6 c.c) and concentrated sulphuric acid (15 c.c.) was gradually added drop by drop and the solution stirred for 1 hour more. The solution was poured into ice and the reddish yellow precipitate was collected and crystallised from glacial acetic acid. By repeated crystallisations from glacial acetic acid two products were obtained: one melting at 245°, yield 8 g. and the other m.p. 220, yield 1 g. The product melting at 245° is 8-nitro-7-hydroxycoumarin and is identical with Clayton's compound (*J. Chem. Soc.*, 1910, **97**, 1400). (Found: N, 7·0. Calc. for $C_9H_5O_5N$: N, 6·76 per cent). The *acetyl* derivative, prepared in the usual manner, crystallised from glacial acetic acid, m.p. 185°. The second product melting at 220° is 6-nitro-7-hydroxycoumarin. (Found: N, 6·91. $C_9H_5O_5N$ requires N, 6·76 per cent). The *acetyl* derivative, prepared as usual, crystallised from acetic acid, m p. 180°, the m.p. being considerably depressed when mixed with the acetyl derivative of 8-nitro-7-hydroxycoumarin.

8-*Amino-7-hydroxycoumarin* was obtained from 8-nitro-7-hydroxycoumarin (7·3 g.) by heating with stannous chloride (24 g.) concentrated hydrochloric acid (20 c.c.) and rectified spirit (20 c.c.). 40 C.c. of hydrochloric acid were then added and the solution allowed to cool when colourless crystals of double salt separated. These were

filtered, dissolved in a small quantity of water and the tin removed by sulphuretted hydrogen. The filtrate was gently warmed and sodium acetate added till precipitation was complete. A greenish substance was obtained, which crystallised from alcohol in yellow needles, m.p. 248-50°. (Found: N, 7·94. $C_9H_7O_3N$ requires N, 7·9 per cent).

8-Chloro-7-hydroxycoumarin.—8-Amino-7-hydroxycoumarin was diazotised in the usual way and the diazo solution treated with cold cuprous chloride solution, when nitrogen was evolved and a red precipitate separated. It was collected, washed with concentrated hydrochloric acid and then with water and crystallised from glacial acetic acid in light yellow needles, m.p. 263°. (Found: Cl, 18·3. $C_9H_5O_3Cl$ requires Cl, 18·06 per cent). The condensation product of chlororesorcin and malic acid melts at 271° (Chakravarti and Ghosh, *loc. cit.*).

Preparation of chlororesorcylaldehyde.—Dry hydrochloric acid gas was bubbled for 2 hours through a solution of chlororesorcin (25 g.) in dry ether (200 c.c.) containing anhydrous zinc cyanide (40 g.), the solution being cooled in a freezing mixture and stirred with a mercury-seal stirrer. The ether was decanted and the solid mass was refluxed with water on a water-bath. On cooling a red solid separated from which chlororesorcylaldehyde was obtained by repeated crystallisation from water as light yellow needles, m.p. 100°, yield 12 g.

Preparation of 6-chloroumbelliferone from chlororesorcylaldehyde.—Dicarbomethoxychlororesorcylaldehyde, m. p. 58°, was obtained in quantitative yield by treating a solution of chlororesorcylaldehyde in *N*-NaOH with methyl chlorocarbonate in the cold. The crude dicarbomethoxy derivative (2 g.) and malonic acid (2 g.) were dissolved in glacial acetic acid (2 c. c.) and heated on a boiling water-bath for 10 hours. The cold solution was diluted with water and the precipitate consisting of dicarbomethoxycinnamic acid and carbomethoxy-umbelliferone carboxylic acid was treated with 10% potassium bicarbonate solution under ice-cooling, when the cinnamic acid passed into solution and the coumarin remained insoluble (*cf.* Mitter and Saha, *loc. cit.*). The insoluble carbomethoxychloroumbelliferone carboxylic acid was boiled with an excess of 10% sodium carbonate solution for 10 minutes. A highly fluorescent solution was obtained which on acidification with hydrochloric acid (1:1) gave a precipitate of umbelliferone carboxylic acid, which crystallised from alcohol,

m. p. 284°. When heated to about 260°-270° in a metal bath chloroumbelliferone began to sublime as colourless prisms, m. p. 271° (mixed m. p. with 6-chloroumbelliferone, the condensation product of 4-chlororesorcin with malic acid is also 271°).

In conclusion our grateful thanks are due to Prof. P. C. Mitter for giving full facilities to carry on this investigation.

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A Semi-micro Method of Determining Total Nitrogen of Air-dry Soils.

BY KALI PADA BASU AND SACHINDRA NATH SARKAR.

The present investigation was undertaken with a view to find out if Pregl's Micro-Kjeldahl method (Fritz Pregl, "Die Quantitative Organische Micro Analyse," 1930, p. 120) could be applied in the determination of the total nitrogen of soils and thus to save time and reagents otherwise necessary for the macro method. In the micro method, it is impossible to work with 3-5 mg. (of the soil) which is the amount usually employed in micro analyses of pure organic compounds due to the almost negligible amount of ammonia that would be obtained. Hence 0·5 g. of the soil was found to be the suitable quantity. Elimination of sampling error, however, is to be carefully guarded against. An experiment was carried out with stock soil to test the method.

EXPERIMENTAL.

About 1 lb of soil was sieved through a 1 mm. sieve and a subsample containing about 50 g. was made in the usual way. The subsample was thoroughly ground in an agate mortar and sieved through a 30 mesh sieve, the process of grinding being repeated until all the soils passed through the sieve. Now the finely ground soil was spread over a glazed paper in thin layer and mixed thoroughly. With the help of a fine nickel spatula, about 0·5 g. of soil taken from different places was weighed in micro weighing bottles, and taken in a micro Kjeldahl digestion flask and about 0·5 g. of sodium sulphate

containing a trace of copper sulphate together with 1 c. c. of water and 2 c. c. of concentrated sulphuric acid. The mixture was then digested in the usual way for about one hour after which it was cooled and 1 c. c. of water added. The digested mass was then transferred to the micro distillation flask and the distillation of ammonia carried out in the apparatus of Parnas and Wagner fully described by Pregl (*loc. cit.*, p. 123). The volume of distilled water employed to transfer the digested mass to the distillation flask was 15 c.c., 10 c.c. of 50% caustic soda solution were employed to make the acid solution in the distillation flask alkaline and the distillation was carried out for 8 minutes. During the last minute of distillation, the end of the silver tube was raised slightly above the level of the standard acid solution in the quartz receiver. A series of estimations was carried out. The results obtained are given in Table I.

TABLE I.

Quantity of soil (*g.*)	...	0·5225	0·5305	0·5699	0·5150
Nitrogen (%)	...	0·0927	0·0922	0 0926	0·0919
				Mean	0·0924
By macro method					0 0933

It is clear from the above table that there is a good agreement between the individual micro determinations indicating thereby that the sampling error has practically been eliminated. Further the small difference between the micro and macro det rminations lies within the limits of experimental error. Next the determination of total nitrogen of Dacca and Faridpur soil was carried out and the results obtained are given in Table II.

TABLE II.

Soil.	Method of estimation.	Nitrogen.	Mean.
Faridpur (alluvial)	Micro	0 0625%	0 0623
		0·0620	
	Macro	0·0627	
Dacca (laterite)	Micro	0·0958	0·0955
		0·0952	
	Macro	0 0960	

Our thanks are due to Prof. J. C. Ghosh for his interest in this investigation.

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The Ionic Susceptibilities of Rubidium from its Different Salts in the Solid and in the Dissolved State.

By S. S. Bhatnagar, M. B. Nevgi and Mohan Lal Khanna.

The ionic susceptibilities for rubidium obtained by different authors* are not consistent. The theoretical values obtained by Pauling, Stoner, Slater, and Angus are 35·0, 30·12, 25·8 and 24·05 respectively, while those obtained experimentally by Pascal, Kido, Ikenmeyer and Abonnenc are 27·2, 27·2, 31·3 and 25·0. (The values refer to $-\chi \times 10^6$). The present investigation has been undertaken to investigate into the causes of these discrepancies which may be ascertained from a knowledge of the values of χ for the rubidium ion from its salts in the solid and dissolved state and the influence of temperature on them. The susceptibilities under different conditions are also capable of yielding information regarding the sizes of molecular diameters and use has been made of the data in settling the well known controversy between the various authors as to whether or not the radii of the rubidium ion in the solid and the dissolved state are different. There have been many contributions to the subject, both theoretical and practical. For example, Joos, Ikenmeyer, Reicheneder and Weiss have determined the ionic diamagnetic values of K, Cl, Cs, I, halogens and H ions. Hecart, Farquharson, Kido and Scott and Blair have also made notable contributions in this domain.†

The general expression for the diamagnetic susceptibility of a symmetrical atom or ion, which is due to Langevin (*Ann. chim. Phys.*, 1905, **5**, 70), is

* Pauling (*Proc. Roy. Soc.*, 1927, **A**, **114**, 181); Stoner (*Proc. Leeds Phil. Soc.*, 1929, **1**, 484); Slater (*Phys. Rev.*, 1930, **36**, 58); Angus (*Proc. Roy. Soc.*, 1932, **A**, **136**, 569); Pascal (*Compt. rend.*, 1913, **156**, 323; 1915, **158**, 37); Kido, (*Sci. Rep. Tohoku Imp. Univ.*, 1932, **21**, 149; 1933, **22**, 235); Ikenmeyer (*Ann. Phys.*, 1929, **1**, 169); Abonnenc, (*Compt. rend.*, 1934, **198**, 2237).

† Joos (*Z. Physik*, 1923, **19**, 347; 1925, **23**, 835); Ikenmeyer. (*loc. cit.*); Reicheneder, (*Ann. Physik*, 1929, **3**, 58); Weiss, (*J. Phys.*, 1930, **1**, 185; *Compt. rend.*, 1930, **190**, 95); Hocart (*Compt. rend.*, 1929, **188**, 1151); Farquharson, (*Phil. Mag.*, 1931, **12**, 283); Kido, (*loc. cit.*); Scott and Blair, (*J. Phys. Chem.*, 1933, **35**, 475).

$$\chi = -\frac{Ne^2}{6mc^2} \Sigma_n \bar{r}^2$$

where $\bar{r}$ is the average distance of the electron from the nucleus or the time average value. The result is not modified except in respect of the different treatment of electron position co-ordinates such as $\bar{r}$. Van Vleck (*Phys. Rev.*, 1928, **31**, 587) and Pauling (*loc. cit.*) have independently calculated the value of $\bar{r}$. An extension of Pauling's work has been made by Gray and his collaborators (*Phil. Mag.*, 1930. **10**, 191; 1931, **11**, 81). Using Hartree's space-charge distribution method (*Proc. Camb. Phil. Soc.*, 1928, **24**, 89), Stoner (*loc. cit.*) has deduced a number of ionic susceptibilities. However, the theoretical values obtained so far are much higher than those obtained experimentally. Zener (*Phys. Rev.*, 1930, **36**, 57) has shown that the nodes in a wave function are unimportant. Slater (*loc. cit*) has made use of this and calculated the mean square radius of the inert gases. Brindley (*Phil. Mag.*, 1931, **11**, 786) has shown that the ionic susceptibilities calculated according to the Slater's formula are in better agreement with the experimental results than those of Pauling or Stoner (*loc. cit.*). Recently Angus (*loc. cit.*) has modified the Slater's formula and found that it gives values which are in good agreement with the experimental results.

A comparative study of the whole subject, particularly with a view to settle the controversy mentioned above, has been undertaken in this investigation.

Experimental.

The apparatus employed during this investigation is a modified form of Decker's balance (Bhatnagar, Nevgi and Tuli, *Indian J. Phys.*, 1935, **9**, 311). In order to determine the susceptibilities at different temperatures, the portion of the tube between the upper stop-cock and the glass window is double-jacketted with an inlet and outlet for the circulation of water at different temperatures. The lower end of the tube carries two stop-cocks between which is fused a side-tube which serves the purpose of introducing the liquid under investigation. Sufficient care was taken to prevent the pole-pieces from getting heated. However, it is just likely that the ends of the pole-pieces might be absorbing some heat and thereby the field might be decreased to some extent. In order to do away with this source of error,

readings with the standard subtances, *i.e.*, water and air, were taken separately at the two temperatures for calculating the values of the specific susceptibility at two different temperatures. In order to ensure that the liquid to be investigated has attained the temperature of hot water circulating round it, water was allowed to circulate for a sufficiently long time before taking the readings. In order to be more sure about it, the susceptibilities of copper sulphate and copper chloride solutions were determined at two different temperatures and therefrom the value of the higher temperature was calculated.

TABLE I.

Substance.	Temperature	
	Calc.	Obs.
Copper sulphate	59·5°	60°
Copper chloride	59·7°	60°

The agreement between the observed and the calculated values clearly shows that the solution in the tube always acquires the temperature of the circulating water. The specific susceptibility in the dissolved state has been calculated according to the following equation (*cf.* Bhatnagar, Nevgi and Tuli, *loc. cit.*):

$$\chi_l = \frac{\phi_l \left[\frac{\chi_w - \chi_a}{\phi_w - \phi_a}\right] + \left[\frac{\chi_a \phi_w - \chi_w \phi_a}{\phi_w - \phi_a}\right]}{d}$$

where χ_l denotes mass susceptibility of the solution, χ_a, that of the air, χ_w, that of the water; ϕ_l, angle of torsion due to the solution, ϕ_a, that one to air, ϕ_w due to water, d, the density of the solution.

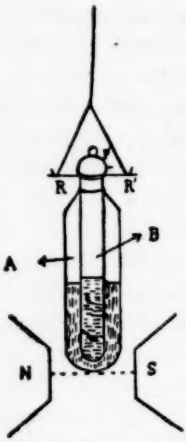
The specific susceptibility of the salt from that of the solution has been calculated with the help of the relation:

$$\chi_l = \chi_{\text{salt}} \times C_{\text{salt}} + \chi_{\text{solvent}} (1 - C_{\text{salt}}).$$

where C_{salt} denotes the concentration of the salt in solution.

The specific susceptibility of the salts in the solid state has been determined by a suitably modified form of Guoy's balance.

The apparatus consisted of a very sensitive weighing balance on a hollow wooden box. The left pan of the balance was replaced by a half pan similar to the one generally used in the specific gravity determination of lighter bodies. To the bottom of this pan was soldered a hollow cylinder which carried a movable hook carrying a fine glass suspension. By means of the hook, the suspension could be raised up or lowered down. Just below the hook, there is a small hole in the base of the balance through which a fine glass thread two feet in length passes. The lower end of the glass thread has a stirrup-like arrangement, while its upper end is attached to the hook and fixed with the help of the sealing wax. The portion of the suspension fibre between the base of the balance and the box is protected from disturbances due to the air-draughts by inserting a glass tube of 3″ in diameter.



The sample tube consists of two tubes A and B; the latter acts as a stopper to the former. B is sealed and contains the paramagnetic substance. The tube is made to hang in the glass stirrup by means of two fine glass fibres R and R′, projected at the top of the tube. In order to keep the tube B in the same position with respect to A, the projected fibre P′ in the sealed tube B is always made to coincide with the projected fibre R′ of the tube A. Secondly in order to keep the whole system in the same position with respect to the magnet, a small mirror is placed behind the tube. In front of this mirror a thin wire-gauze is placed (A mark P is made in the tube A.). By means of the parallax method, the tube is placed in the same position every time. The lower end of the specimen tube comes in between the poles of the big electromagnet as shown in the figure. At first the pull due to the paramagnetic substance only is noted and then the combined pull due to para as well as diamagnetic substances together is read (care being taken that the combined pull should be of attraction). By subtracting the combined pull from that due to the paramagnetic substance only, one can easily find out the repulsion due to the diamagnetic substances.

The force acting on the cylinder along its axis is given by

$$F_x = (\chi_1 m_1 - \chi_2 m_2) H_y \frac{\partial H_y}{\partial x} \quad \ldots \quad \ldots \quad (i)$$

where χ_1 and χ_2 are the mass susceptibilities of the substance and the medium and m_1 and m_2 are the masses of the specimen and the medium occupying the same volume as the specimen respectively. If W_g is the pull due to the empty tube only, then

$$W_g = (\chi_g m_g - \chi_a m_{a\cdot g}) H_y \frac{\partial H_y}{\partial x} \quad \ldots \quad \ldots \quad \ldots \quad (ii)$$

where χ_g denotes the mass susceptibility of the glass tube, χ_a that of the medium, m_g and $m_{a\cdot g}$ are the mass of the glass tube and of the medium displaced by the glass tube. If W_p is the additional pull due to the paramagnetic substance, then

$$W_g + W_p =$$

$$\left[(\chi_p m_p + \chi_g m_g) - \chi_a (m_{a\cdot g} + m_{a\cdot p}) \right] H_y \frac{\partial H_y}{\partial x} \quad \ldots \quad (iii)$$

where x_p denotes mass susceptibility of the paramagnetic substance, m_p, mass of the paramagnetic substance, $m_{a\cdot p}$, mass of the medium displaced by the paramagnetic substance.

If W_{d_1} is the pull due to the diamagnetic substance then

$$W_g + W_p + W_{d_1} = \left[(\chi_g m_g + \chi_p m_p + \chi_{d_1} m_{d_1}) - \chi_a (m_{a\cdot g} + m_{a\cdot p} + m_{a\cdot d_1}) \right] H_y \frac{\partial H_y}{\partial x} \quad \ldots \quad (iv)$$

Subtracting (*iii*) from (*iv*) it gives:

$$W_{d_1} = \left(\chi_{d_1} m_{d_1} - \chi_a m_{a\cdot d_1} \right) H_y \cdot \frac{\partial H_y}{\partial x} \quad \ldots \quad (v)$$

Similarly the pull due to some other diamagnetic substance d_2 can be found out and

$$W_{d_1} = \left(\chi_{d_1} m_{d_2} \chi_a \cdot m_{a\cdot d_2} \right) H_y \cdot \frac{\partial H_y}{\partial x} \quad \ldots \quad (vi)$$

Dividing (*v*) by (*vi*)

$$\frac{W_{d_1}}{W_{d_2}} = \frac{\chi_{d_1} m_{d_1} - \chi_a m_{a \cdot d_1}}{\chi_{d_2} m_{d_2} - \chi_a m_{a \cdot d_2}}$$

$$\therefore \quad x_{d_2} = \frac{1}{m_{d_2}} \left[\left(\chi_{d_1} m_{d_1} - \chi_a m_{a \cdot d_1} \right) \frac{W_{d_2}}{W_{d_1}} + \chi_a m_{a \cdot d_2} \right] \qquad (vii)$$

This equation has been used for calculating the susceptibilities of the substances under investigation.

The calculations given above hold when both the substances are in the inhomogeneous field ; but even if part of the tube containing the paramagnetic material is in the inhomogeneous and the diamagnetic in the homogeneous field, the final formula will hold as the method is a purely substituted one and is independent of the field gradient.

For higher temperature measurements, an electric oven made of mica pieces and nichrom wire was used. In order to avoid the changes in the field that might perhaps be produced near the pole pieces, the readings for the standard substances were repeated at higher temperatures and were found to be the same as those at the lower temperatures. In order to see whether the substances in the tube had attained the temperature recorded by the thermometer in the electric furnace, anhydrous copper sulphate and cobalt sulphate were tried and from the Curie-Weiss law,

$$\chi_M = \frac{C_M}{T - \theta}.$$

the values of temperature were calculated.

TABLE II.

Substance.	Temperature.	
	Calc.	Obs.
Copper sulphate (anhydrous)	89·4°	90°
Cobalt sulphate (anhydrous)	89·6°	90°

The agreement between the observed and the calculated values of temperatures justifies the above assumption.

As the purity of the substances employed is of great importance, Merck's extra pure rubidium salts were used during this investigation. The results are shown in the tables below.

TABLE III.

Salt.	$-\chi \times 10^6$ at 30° solid.	$-\chi \times 10^6$ at 20° solution.	$-\chi \times 10^6$ ionic (solid).	$-\chi \times 10^6$ ionic (solution).
RbCl	0·386	0·386	26·45	26·68
RbBr	0·346	0·347	26·63	26·78
RbI	0·336	0·337	26·76	26·97
Rb_2SO_4	0·331	0·331	27·38	27·38

TABLE IV.

Temperature effect.

Salt.	Solid		Solution	
	$-\chi \times 10^6$ at 30°.	$-\chi \times 10^6$ at 60°.	$-\chi \times 10^6$ at 20°.	$-\chi \times 10^6$ at 60°.
RbCl	0·385	0·390	0·386	0·395
RbBr	0·346	0·350	0·347	0·351
RbI	0·336	0·340	0·337	0·345
Rb_2SO_4	0·331	0·335	0·331	0·336

DISCUSSION.

Many interesting points arise out of the results described in this paper. The general expression for the ionic susceptibility is

$$\chi_{ion} = -\frac{N e^2}{6m e^2} \sum_n \bar{r}^2 = 2{\cdot}832 \times 10^{10} \sum \bar{r}^2$$

If in this expression the value of χ_{ion} for rubidium is substituted, the ionic value for radius of the rubidium ion can be easily calculated and is equal to $1{\cdot}875 \times 10^{-8}$ cm. Scott (*J. Phys. Chem.*, 1931,

35, 1410), Pauling (*loc. cit.*), Goldsmidth (*Trans. Faraday Soc.*, 1929, **25**, 282) and Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589) have obtained the ionic radius of rubidium from the different states of rubidium salts. The values obtained by them are given in Table V.

TABLE V

Ionic radius of rubidium.

Author.	State.	Ionic value.
Scott	Saturated solution	$1{\cdot}37 \times 10^{-8}$ cm.
Pauling	Theoretical, crystalline state	$1{\cdot}48 \times 10^{-8}$
Goldsmidth	Empirical, crystalline state	$1{\cdot}49 \times 10^{-8}$
Webb	Dilute solutions	$2{\cdot}02 \times 10^{-8}$
Present authors.	Solid as well as dissolved state	$1{\cdot}875 \times 10^{-8}$

The value $1{\cdot}875 \times 10^{-8}$ cm obtained is approximately mid-way between the two sets of values given above.

The ionic diamagnetism of rubidium ion is the same in the solid as well as in the dissolved state. It is obvious that if the numerical value of χ_{ion} remains the same in the equation given above, the ionic value for the radius also remains the same. The magnetic measurements support the view put forward by Kazimierz Jablczynski (*Rocz. Chem.*, 1923, **18**, 883, 91) and Abonnenc (*loc. cit.*) that the ionic dimensions are the same in different states as against that of Scott (*loc. cit.*) who is of the opinion that the ionic radius of rubidium is different in different states. The ionic value for the radius of rubidium in the saturated solution is 1·37 while in the dilute solution it is $2{\cdot}02 \times 10^{-8}$ cm.

The physical and chemical properties of the rubidium salts, such as solubility, viscosity and refractive index, are in favour of the above mentioned view, namely, the radius of rubidium ion does not change in different states. Rubidium does not form any complexes such as hydrates which would have been responsible to some extent for changing the ionic radius and thereby the ionic diamagnetism of rubidium.

In Table VI the experimental as well as theoretical ionic diamagnetic values of rubidium found by various authors are tabulated.

TABLE VI.

Ionic diamagnetic values.

Theoretical.

Pauling.	Stoner.	Slater.	Angus.
35·0.	30·12	25·8	24·08

Experimental.

Pascal,	Ikenmeyer.	Kido.	Abonnenc.	Present authors.
27·2	31·3	27·2	25·0	26·93

These values refer to $-\chi \times 10^6$.

The ionic values obtained closely correspond with the values obtained by Pascal (*loc. cit.*) and Kido (*loc. cit.*). Temperature has practically no influence on the diamagnetism of the rubidium salt.

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Solubility of Benzoic and Salicylic Acids in Mixtures of Organic Solvents.

By P. G. Desai and A. M. Patel.

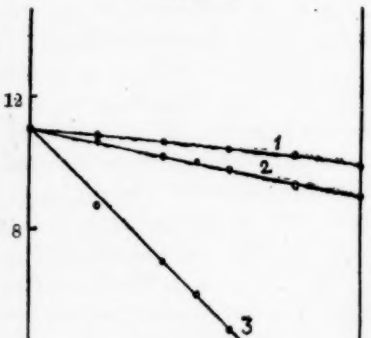
It seems that very little work seems to have been undertaken with a view to study the behaviour of three types of mixtures namely (*i*) two comparatively non-polar, (*ii*) polar and non-polar, and (*iii*) two polar solvents, on the solubility of organic acids.

With a view to study the three types of mixtures on the solubility of benzoic and salicylic acids, the present work was undertaken. The same method described by the authors (*J. Indian Chem. Soc.*, 1935, **12**, 131), was followed for the estimation of the solubilities of the organic acids.

Results and Discussion.

In Figs. 1-6 are plotted the results of the solubility of benzoic acid in mixtures containing varying amounts of organic solvents. It can be seen from Fig. 1 where the solubility of the acid in mixtures of two non-polar liquids is plotted, that the curves are almost straight lines.

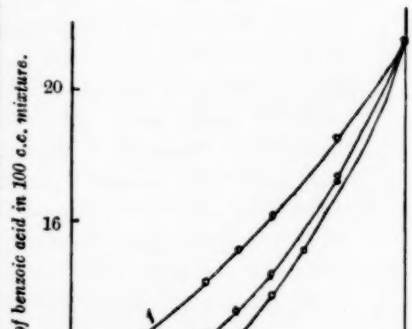
Fig. 1.



Pereentage of benzene.

Curves 1—3 refer to mixtures of benzene with tolune, xylene and hexane respectively.

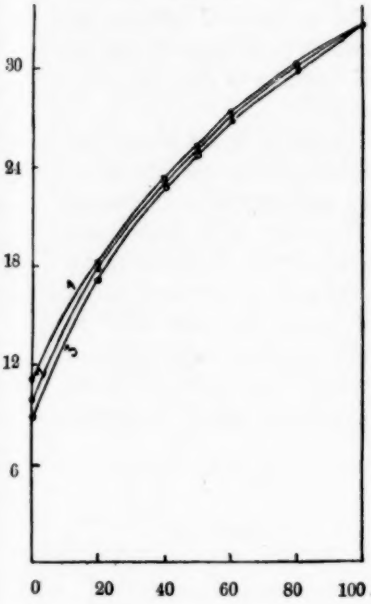
Fig. 2.



Percentage of chloroform.

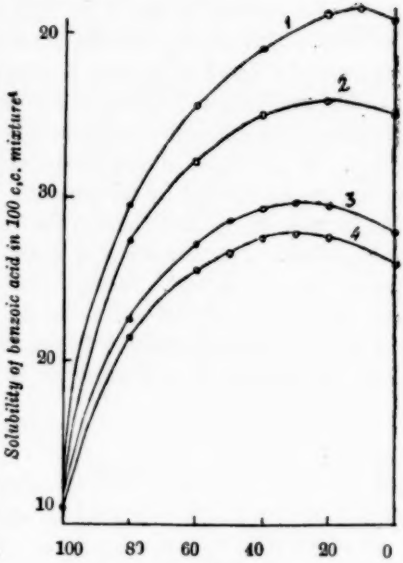
Curves 1—3 refer to mixtures of $CHCl_3$ with benzene, toluene and xylene respectively.

FIG. 3.



Curves 1—3 refer to mixtures of acetone with benzene, xylene and toluene respectively

FIG. 4.



Curves 1—4 refer to mixture of benzene with MeOH, EtOH *n*-PrOH and *n*-BuOH respectively.

This linear relation is due to the fact that when two non-associated liquids are mixed, very small volume and temperature changes occur (*cf.* Walker and Henderson, *Trans. Roy. Soc. Canada*, 1902, **105**, 8). These results are also in agreement with the conclusion arrived at by Padoa and Mattencci, (*Atti. R. Accad. Leiniceir* 1914, **23**, 590) from their work on the surface tension of a mixture of benzene and toluene. The nature of the curves obtained when salicylic acid was used as a solute was the same as that in the case of benzoic acid.

Chloroform which is slightly polar seems to act in an abnormal manner as can be seen from Fig. 2. The solubility of the acid in its presence is less than what it should be according to the simple mixture rule. It is probable that it makes a very loose complex with the solute and the effect of the addition of an aromatic hydrocarbon is to inhibit this formation.

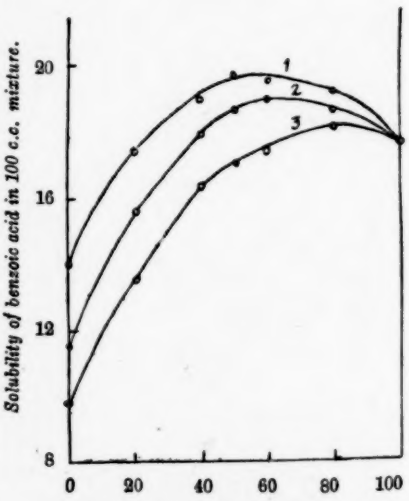
When acetone which is polar in nature is used as a component of the mixture with the aromatic hydrocarbons, the curves are convex to the concentration axis of the mixture. The presence of acetone increases the solvent power of the hydrocarbons on account of its polar character. This accounts for the increased solubility of the acid. The same was also found in the case of salicylic acid.

The solubilities of benzoic acid in mixtures of benzene as one component and different alcohols as other components are plotted in Fig. 4. In mixtures of the above type, the non-polarity of benzene will be greatly affected by the presence of strongly polar alcohols and this, in turn, will greatly increase the solvent action of the aromatic hydrocarbon. This increase is in accordance with the solvent power of alcohols on benzoic acid. Methyl alcohol which has been found to have the greatest solvent action on the acid increases the solubility of the acid to approximately 1·7 times that calculated according to the ideal mixture rule for a mixture of 80% benzene and 20% methyl

FIG. 5.

Curves 1—4 refer to mixtures of nitrobenzene with MeOH, EtOH, *n*-PrOH and *n*-BuOH respectively.

FIG. 6.



Curves 1—3 refer to mixtures of nitrobenzene with benzene, toluene and xylene respectively.

alcohol, whereas ethyl alcohol increases it 1·66 times. Other alcohols increase it to a smaller extent. This is due to the fact that the solvent action of benzene is increased proportionately to the polarity of the alcohols. The same was found when toluene and xylene were used along with the fatty alcohols. In the case of salicylic acid also, identical results were obtained.

In all the four curves, there are maxima showing that the solubility of the acids at these points is the highest. In the case of methyl alcohol, the maximum occurs at the composition of the mixture containing 90% alcohol and 10% benzene, while in the case of ethyl, *n*-propyl and *n*-butyl alcohols, the maxima occur at 80%, 70% and 70% alcohols respectively. Wagner (*Z. physikal. Chem.*, 1903, **46**, 867) and Dunstan (*J. Chem. Soc.*, 1904, **85**, 817) have shown that a minimum in the viscosity-composition curve of a mixture of benzene with *n*-propyl alcohol and benezene and ethyl alcohol is obtained. They, therefore, deduce that under these circumstances, some de-association has resulted. The maxima in Fig. 4, therefore, indicate the maximum suitable polarity of the mixtures with respect to the nature of the solute.

The results of solubilities of benzoic acid in mixtures of nitrobenzene and alcohols which are plotted in Fig. 5 are very interesting. Both the components of the mixture are polar in character. The solvent action of nitrobenzene is less than that of the alcohols because the polarity of the solute is less than that of nitrobenzene. At any composition of the mixture, the solubility of the acid is greater than what is calculated from the ideal mixture rule. The nature of the curves in Fig. 5 is the same as that in Figs. 4 and 6. These results emphatically indicate that whenever a highly non-polar or highly polar solvent is used along with alcohols as one of the components of the mixture, maxima in the solubility-composition curves are always obtained. As mentioned before, this can be explained on the assumption that the more polar component of the mixture under these circumstances undergoes partial de-association.

Various predictions for the nature of solubility curves for different mixtures of solvents can also be made for different solutes. Thus the solubility curves of any solute in mixtures of aromatic hydrocarbons which are very slightly polar will be straight lines. Similarly, it is to be expected that when the constituents of a binary mixture resemble one another, as in the case of mixtures of methyl with ethyl alcohol and ethyl with propyl alcohol, the solubility should follow the mixture rule.

Summary.

1. Solubilities of benzoic and salicylic acids have been determined in different binary mixtures of varying compositions.

2. The effect of mixtures of non-polar with non-polar, non-polar with polar and polar with polar solvents on the solubility of benzoic and salicylic acids has been studied.

3. It is shown that in mixtures of non-polar solvents as both the components, the solubility-composition curves are straight lines.

4. The solubility in chloroform decreases as it is diluted more and more by the addition of aromatic hydrocarbons. The solubility-composition curves are convex to the axis of composition.

5. It has been shown that the solubility in acetone decreases as it is diluted more and more by the addition of non-polar solvents such as benzene, toluene, *m*-xylene.

6. It has been shown that the solubility in alcohols first increases, reaches a maximum and then deceases as they are more and more diluted by the addition of aromatic hydrocarbons or nitrobenzene. The same is found when mixtures of nitrobenzene with different aromatic hydrocarbons are used as solvents.

7. The behaviour of salicylic acid is the same as that of benzoic acid in the same binary mixtures.

8. It has been shown that the general nature of the curves remains the same, no matter in what way the solubility or the composition of the mixture is expressed.

The authors wish to thank Professor A. R. Normand for his continued interest in the work.

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Note on the Constitution of Formic Acid and Formates.

By R. M. Halasyam.

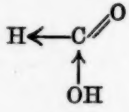
Much speculation has centered round the question of the constitution of formic acid and its salt (Ray, *Nature*, 1934, **133**, 646; and Sarkar and Ray, *Proc. Indian Science Congress*, 1935, p. 109). These investigators advance the view that the acid molecule has the structure $H\leftarrow\underset{\uparrow}{\underset{OH}{C}}=O$, while the ion the structure $:\underset{\uparrow}{\underset{OH}{C}}=O$ on the grounds of the large difference in properties of the non-ionised acid and the acid residue. It is pointed out that this structure brings to the fore-ground the particular reducing character of the formate ion, which has a lone pair of electrons, in contrast to the acid molecule or its esters. Thus it is the hydrogen attached to the carbon atom that ionises, but not the one in the hydroxyl group, which once again distinguishes formic acid from its higher analogues, *i.e.*, acetic or butyric acids. In further support of this view it is shown that cadmium formate does not give rise to the Raman line 2930,* corresponding to the C – H linkage and present in formic acid, and that the metallic formates and nitrites exhibit isomorphic relations, especially in their barium and strontium compounds.

Seshadri (*Current Science*, 1934, **3**, 353) disagrees with this view and postulates in its place a labile structure) to the acid molecule, $H-C\overset{O}{\underset{OH}{<}} \rightleftharpoons :C\overset{OH}{\underset{OH}{<}}$ which is apparently meant to do away with the heterodox hypothesis of Ray and Sarkar and yet explain the absence of the well known Raman line.

* It is interesting to note also that Ghosh and Kar (*J. Phys. Chem.*, 1935, **35**, 1735) studied the Raman-spectra of sodium formate solution and noticed the absence of the Raman-shift $\Delta\nu = 2930$ whereas in solution of sodium acetate, this Raman-shift was easily detected.

The work of Sheibler on compounds like $C(OC_2H_5)_2$ and $C(ONa)(OC_2H_5)$ is cited in support of the dihydroxymethylene structure. While it is true that the lone pair of electrons belonging to the C− atom may endow it with special reducing properties, one is inclined to ask the very pertinent question how this structure with two equivalent hydrogen atoms can satisfy the avowedly monobasic character of the acid. The labile structure is more in the nature of a zealous endeavour to save the classical formulæ of organic chemistry from the ruthless onslaughts of the modern physical chemist with hiss earching *X*-ray and spectroscopic analysis. It is prabably once again this fervour which actuated the statement, " If this could be proved, (the ionisation of the hydrogen atom in the C−H linkage) formic acid would become not only exceptional among the fatty acids, but would hold a unique position among all organic compounds,' in the face of unequivocal evidence from Raman spectra and isomorphism of formates and nitrites.

Further evidence for the new type of formic acid molecule may be advanced on considerations of the parachor. Adopting the improved Mumford and Philips values for the various atoms and the singlet, doublet and semi-polar bonds, the parachor for the

structure  works to 93·6 units while that for the

structure to 78·7 units. The former value is so much

in agreement with that calculated from data on surface tension, *i.e.*, 93·9 units that one is tempted on this ground alone to adopt the new structure.

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